Supplementary Information (SI) for Green Chemistry.

Supplemental Information

Photocatalytic Radical (O)P─P(O) Bond Formation: Access to Diphosphine Dioxides for Thermosets Protection

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1. General information

1.1 Materials

All reactions were carried out in an open - air atmosphere using standard techniques. All reagents and materials were commercially available and used as received, unless otherwise noted. Diglycidyl ether of bisphenol A (DGEBA) with epoxy resin value of 0.44 mol/100 g was purchased from Nantong Xingchen Synthetic Material Co., Ltd., China. 4,4-diaminodiphenyl methane (DDM) were purchased from Titan Technology Co., Ltd., China. Polyether polyols (average molecular weight of 4800, average functionality of 3.0, and hydroxyl value of 35 mg of KOH/g) were purchased from Zibo Dexin Federal Chemical Industry Co., Ltd., Zibo, China. The catalysts (bis(dimethylaminoethyl) ether, and dibutyltin dilaurate), pore-forming agent, and surfactant were all sourced from Tianjin Qiyue New Materials Co., Ltd., Tianjin, China. Triethanolamine was purchased from Kelong Chemical Regent Factory, Chengdu, China. Modified 4,4'-diphenylmethane diisocyanate (MDI, NCO content is 26.5%) was obtained from Huntsman Chemical Trading Co., Ltd., Shanghai, China. The RLH-18HC-B photo reactor set-up (455 nm) was supported by Beijing Bibby scientific Co., Ltd., China. All solvents were purchased in anhydrous form with a purity of ≥99.9% and used as received. Distilled water was obtained from our laboratory.

1.2 Characterization

Melting points were obtained on a Yanaco M500 melting point apparatus and are corrected. High-resolution mass spectra were obtained via an Agilent LC/MSD TOF 6500 series mass spectrometer. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance NEO 400 MHz spectrometer (Germany). The instrument was used to acquire ^{1}H NMR (400 MHz), ^{13}C NMR (101 MHz), ^{19}F NMR (376 MHz), and ^{31}P NMR (162 MHz) spectra. Chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane (TMS) as an internal standard in $CDCl_3$ or DMSO-d^6 solutions.

For ^{1}H NMR spectra, chemical shifts are referenced to TMS at 0.00 ppm, residual $CHCl_3$ at 7.26 ppm, or residual DMSO-d^6 at 2.50 ppm. The following abbreviations are used to denote multiplicity: δ = chemical shift, J = coupling constant (Hz), s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet.

For ^{13}C NMR spectra, chemical shifts are referenced to the solvent signal of $CDCl_3$ (77.16 ppm, central peak) or DMSO-d^6 (39.50 ppm, central peak).

Solid-state ^{1}H NMR spectra were acquired on a Bruker Avance 400 MHz spectrometer equipped with a H13925_0025 probe (PH MAS DVT 400W1 BL4 N - P/F - H). The sample was packed into a zirconia rotor and measured at a temperature of 293.7 K (~20.6 °C). A standard one-dimensional single-pulse sequence was employed with the following acquisition parameters: spectral width 81967.2 Hz, pulse width 2.50 μs, relaxation delay 3.00 s, acquisition time 0.0625 s, number of scans 32, and receiver gain 8.0. The free induction decay was collected with 5120 data points and zero-filled to 16384 points prior to Fourier transformation, yielding a final digital resolution of 5.00 Hz/point. Chemical shifts are reported in ppm relative to an external reference standard. All spectra were processed using the TopSpin software suite.

Solid-state ^{31}P NMR spectra were acquired on a Bruker Avance 400 MHz spectrometer equipped with a H13925_0025 probe (PH MAS DVT 400W1 BL4 N - P/F - H). The sample was packed into a zirconia rotor and measured at 294.1 K (~21 °C). A standard one-dimensional cross-polarization (CP) pulse sequence was employed with the following acquisition parameters: number of scans 1024, relaxation delay 2.00 s, pulse width 3.33 μs, spectral width 48543.7 Hz, and acquisition time 0.0422 s. The free induction decay was collected and processed with zero-filling to 16384 points, yielding a final digital resolution of 2.96 Hz/point. The ^{31}P observation frequency was 162.06 MHz. Chemical shifts are reported in ppm relative to an external reference standard. All spectra were processed using the Bruker TopSpin software suite.

Fourier transform infrared (FTIR) spectroscopy was performed on a Nicolet IS10 spectrometer (Thermo Scientific, USA). Samples were homogenized with KBr and pressed into pellets. Spectra were acquired in the range of 4000–400 cm^{-1} by averaging 64 scans at a resolution of 1 cm^{-1}.

Limiting Oxygen Index (LOI) was determined using a JF - 3 oxygen index analyzer (manufactured by Nanjing Jiangning Analysis Co., Ltd.) in accordance with the national standard GB/T 2406.3 - 2022 to evaluate the flame - retardant performance of the material. The test specimens measured 130 mm × 6.5 mm × 3.2 mm. A flame length of 15 mm was applied for ignition. The burning duration was less than 3 minutes, and the burning length did not exceed 50 mm. The reported LOI value represents the concentration at which the material consistently passed the test in at least three consecutive trials.

Vertical Burning Test (UL - 94) was conducted using a CZF - 3 vertical burning tester (manufactured by Nanjing Jiangning Analysis Co., Ltd.) in accordance with the national standard GB/T 2408 - 2021. The test specimens measured 130 mm × 13 mm × 3.2 mm. A Bunsen burner flame (height 20.0 ± 1.0 mm) was applied to the center of the lower edge of each specimen for 10.0 ± 0.5 seconds. For each set of five specimens, the flame application was performed twice consecutively. After flame removal, the afterflame times (t_1 and t_2) and ignition conditions for both applications were recorded separately. The burning time for each specimen is reported as the average of five parallel trials.

Cone Calorimeter (CC) tests were performed using a cone calorimeter from Fire Testing Technology Ltd. (FTT, UK) in accordance with the standard ISO 5660 - 1:2015 to characterize the combustion behavior of the material, at a heat flux of 35 kW/m². The sample dimensions were 100 mm × 100 mm × 3 mm. Each sample group was tested in triplicate, and the results were averaged.

Thermogravimetric analysis (TGA) was conducted using a TGA - 550 thermal analyzer (TA Instruments, U.S.). The samples (5 - 8 mg) were subjected to heating from 40 °C to 800 °C at a variable heating rate of 10 °C/min under a nitrogen atmosphere with a gas flow of 50 mL/min.

Scanning electron microscopy (SEM) was employed for the microscopic morphology analysis. The instrument used was the German ZEISS Gemini 300 scanning electron microscope. The morphology of the cross - section, coated with thin gold layers, was observed under high vacuum conditions at a voltage of 20 kV.

Tensile properties were evaluated according to ISO 1798:2008 using an E44.104 universal testing machine (MTS Systems, China). Specimens were stretched uniformly at a prescribed rate, with simultaneous recording of the applied force and elongation to derive the tensile stress - strain curve. Key parameters, including tensile strength, elongation at break, and tensile toughness, were determined for the foam samples. Additionally, tensile tests were performed on an Instron 5400 universal testing machine (USA) equipped with a 500 N load cell, at a crosshead speed of 500 mm/min and a maximum load of 250 N. Results for each sample group are presented as the mean value obtained from five replicate measurements.

Cyclic compressive tests were conducted using an Instron 5400 universal testing machine (USA) equipped with a 500 N load cell. The specimens were subjected to 100 compression cycles at a maximum deformation of 50% and a constant strain rate of 20 mm/min. Throughout the tests, force and displacement data were recorded to generate compressive stress - strain curves. In addition to determining the compressive strength of the foam, these tests also allowed for the calculation of the corresponding compressive strength recovery rate and compressive deformation recovery rate. Specimens measuring 50 × 50 × 25 mm^3 were used, with three replicate measurements performed for each sample.

Thermal aging (dry - heat aging): Accelerated aging tests were performed on different FPUF samples in accordance with GB/T 9640 - 2008/ISO 2440:1997 to evaluate the changes in mechanical properties during routine use. Dry - heat aging was carried out using a DHG - 9140A oven. For the temperature investigation, the samples were aged at 125 °C for 16 h. The sample dimensions and quantity were the same as those used in the aforementioned mechanical property tests.

UV aging: Ultraviolet (UV) aging tests were conducted on different FPUF samples in accordance with GB/T 16422.3 - 2022/ISO 4892 - 3:2016 to evaluate the changes in their mechanical properties under simulated service conditions. A UVA - 351 lamp (Type 1B) was employed for UV irradiation. During the temperature - related investigation, the irradiance was set at 0.76 W/(m^2 • nm) at 340 nm, and the exposure duration was 24 h. The sample dimensions and quantity were identical to those used in the mechanical property tests described above.

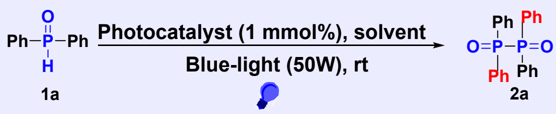
Acid aging: Specimens identical in size and quantity to those described above were immersed in a 1 mol/L hydrochloric acid (HCl) solution for 24 h. After immersion, the samples were removed and dried in an oven at 70 °C.

Alkali aging: Specimens with identical dimensions and quantities to those described above were immersed in a 1 mol/L sodium hydroxide (NaOH) solution for 24 h. Subsequently, the samples were removed and dried in an oven at 70 °C.

Salt aging: Specimens identical in size and quantity to those described above were immersed in a saturated sodium chloride (NaCl) solution for 24 h. The samples were subsequently removed and dried in an oven at 70 °C.

2. Optimization of the reaction conditions

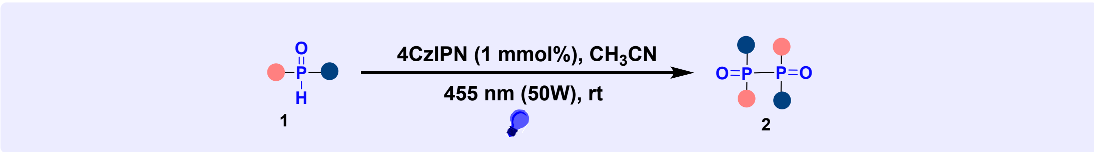
Table S1 Optimization of synthesis conditions for **2a** [a]



Entry	Catalyst	Solvent	Temperature ℃	Time h	Radiation （50W）	Yield [b] %
1	4CzIPN	CH_3CN	25	24	Blue lights	99
2	4CzTPN	CH_3CN	25	24	Blue lights	69
3	Eosin B	CH_3CN	25	24	Blue lights	71
4	Eosin Y	CH_3CN	25	24	Blue lights	73
5	4CzIPN	DCM	25	24	Blue lights	39
6	4CzIPN	DMSO	25	24	Blue lights	53
7	4CzIPN	Xylene	25	24	Blue lights	62
8	4CzIPN	CH_3CN	50	24	Blue lights	99
9	-	CH_3CN	25	24	Blue lights	48
10	4CzIPN	CH_3CN	25	24	-	0
11	4CzIPN	CH_3CN	25	12	Blue lights	55

[a] Conditions: **1a** (0.5 mmol), photocatalyst (1 mmol %) in solvent (2 mL) using 50 W blue LEDs at room temperature for 24 h. [b] Isolated yields.

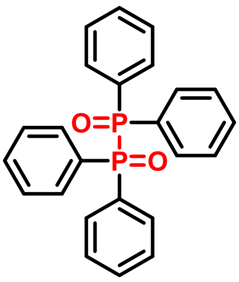
3. General procedure for the preparation of 2a-2m and 4a-4g



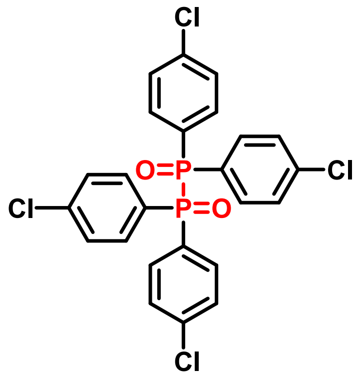
In a 10 mL Schlenk tube equipped with a magnetic stir bar, P(O)H compound **1** (0.5 mmol) and 4CzIPN (7.8 mg, 0.01 mmol) were placed. The system was filled with acetonitrile (2.0 mL). After sealing, the reaction mixture was irradiated with 50 W blue LEDs (455 nm) at room temperature for 24 - 120 h. The product **2** was obtained by filtration. Note: Add K_2CO_3 (0.5 mmol) as a base and the post-treatment step involves directly conducting rotary evaporation to remove the solvent, thereby obtaining the liquid product **2k - 2m**. (The RLH-18HC-B photo reactor set-up (455 nm), which was supported by Beijing Bibby Scientific Co., Ltd., China, is shown in the following picture.)

Figure S1. Photo reactor set-up

Characterization data:

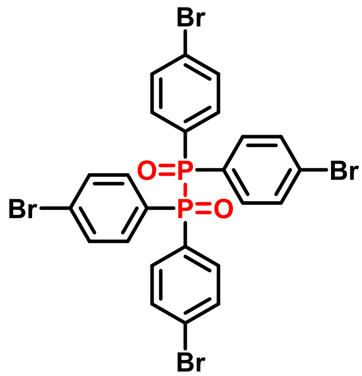


1,1,2,2-tetraphenyldiphosphane 1,2-dioxide (2a) White solid. M.p.: 163.2-164.8 °C , 0.1989 g, 99% yield . ^{1}H NMR (400 MHz, DMSO-d6) δ 7.74 (dd, J = 11.3, 7.5 Hz, 8H), 7.48 (dd, J = 13.2, 6.1 Hz, 12H). ^{31}P NMR (162 MHz, DMSO-d6) δ 23.12. ^{13}C NMR (101 MHz, DMSO-d6) δ 135.6 (d, $J_{P\text{-}C}$ = 134.7 Hz), 131.8 (d, $J_{P\text{-}C}$ = 2.2 Hz), 131.4 (d, $J_{P\text{-}C}$ = 10.0 Hz), 128.9 (d, $J_{P\text{-}C}$ = 12.5 Hz). HRMS (ESI) calcd. For $[(C_{24}H_{20}O_2P_2)+Na]^+$ m/z 425.0831, found 425.0842.



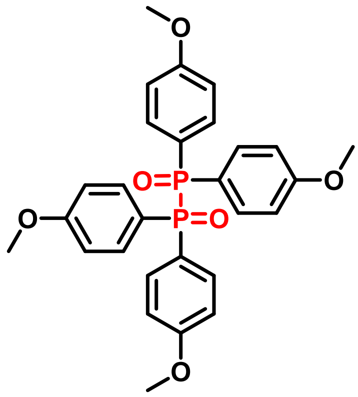
1,1,2,2-tetrakis(4-chlorophenyl)diphosphane 1,2-dioxide (2b)

White solid. M.p.: 129.9-130.5 °C, 0.1035 g, 76% yield. ^1H NMR (400 MHz, DMSO-d6) δ 7.77 – 7.68 (m, 8H), 7.53 (dd, J = 8.4, 2.5 Hz, 8H). ^{31}P NMR (162 MHz, DMSO-d6) δ 21.40. ^{13}C NMR (101 MHz, DMSO-d6) δ 137.2 (d, $J_{P\text{-}C}$ = 3.4 Hz), 134.0 (d, $J_{P\text{-}C}$ = 136.9 Hz), 133.3 (d, $J_{P\text{-}C}$ = 10.9 Hz), 129.2 (d, $J_{P\text{-}C}$ = 13.2 Hz). HRMS (ESI) calcd. For $[(C_{24}H_{20}O_2P_2C_{l4})+NH_4]^+$ m/z 555.9718, found 555.9722.



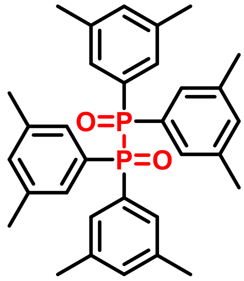
1,1,2,2-tetrakis(4-bromophenyl)diphosphane 1,2-dioxide (2c)

Light yellow solid, M.p.: 140.1-142.8 °C, 0.1625g, 90% yield. ^1H NMR (400 MHz, DMSO-d6) δ 7.73 – 7.59 (m, 16H). ^{31}P NMR (162 MHz, DMSO-d6) δ 21.62. ^{13}C NMR (101 MHz, DMSO-d6) δ 134.4 (d, $J_{P\text{-}C}$ = 136.5 Hz), 133.4 (d, $J_{P\text{-}C}$ = 10.8 Hz), 132.1 (d, $J_{P\text{-}C}$ = 13.0 Hz), 126.2 (d, $J_{P\text{-}C}$ = 3.5 Hz). HRMS (ESI) calcd. For $[C_{24}H_{16}Br_4O_2P_2]^+$ m/z 717.7318, found 717.7313.

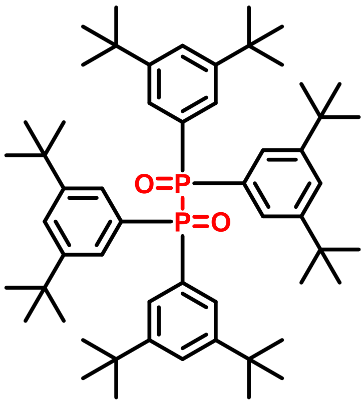


1,1,2,2-tetrakis(4-methoxyphenyl)diphosphane 1,2-dioxide (2d)

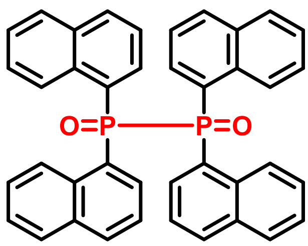
White solid. M.p.: 177.4-180.2 °C, 0.1032 g, 79% yield. ^1H NMR (400 MHz, DMSO-d6) δ 7.64 (dd, J = 11.1, 8.7 Hz, 8H), 7.01 (d, J = 6.9 Hz, 8H), 3.77 (s, 12H). ^{31}P NMR (162 MHz, DMSO-d6) δ 24.19. ^{13}C NMR (101 MHz, DMSO-d6) δ 162.0 (d, $J_{P\text{-}C}$ = 2.8 Hz), 133.2 (d, $J_{P\text{-}C}$ = 11.3 Hz), 127.1 (d, $J_{P\text{-}C}$ = 141.8 Hz), 114.3 (d, $J_{P\text{-}C}$ = 13.5 Hz), 55.7. HRMS (ESI) calcd. For $[(C_{28}H_{28}O_6P_2)+Na]^+$ m/z 545.1253, found 545.1260.



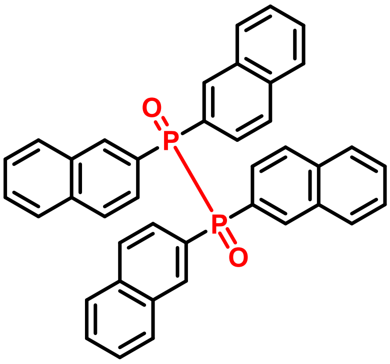
1,1,2,2-tetrakis(3,5-dimethylphenyl)diphosphane 1,2-dioxide (2e) White solid. M.p.: 246.8-247.7 °C. 0.1045 g, 81% yield. ^{1}H NMR (400 MHz, DMSO-d6 and $CDCl_3$) δ 7.31 (d, J = 12.3 Hz, 8H), 7.03 (s, 4H), 2.24 (s, 24H). ^{31}P NMR (162 MHz, DMSO-d6 and $CDCl_3$) δ 26.12. ^{13}C NMR (101 MHz, DMSO-d6 and $CDCl_3$) δ 137.8 (d, $J_{P\text{-}C}$ = 13.4 Hz), 134.6 (d, $J_{P\text{-}C}$ = 134.7 Hz), 133.1 (d, $J_{P\text{-}C}$ = 2.7 Hz), 128.8 (d, $J_{P\text{-}C}$ = 10.1 Hz), 21.3. HRMS (ESI) calcd. For ($[C_{32}H_{36}O_2P_2]$+Na)$^+$ m/z 537.2083, found 537.2085.



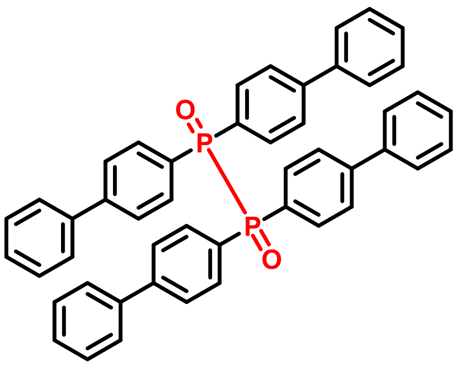
1,1,2,2-tetrakis(3,5-di-tert-butylphenyl)diphosphane 1,2-dioxide (2f) White solid. M.p.: 225.3-227.6 °C, 0.2018 g, 95% yield. ^{1}H NMR (400 MHz, DMSO-d6 and $CDCl_3$) δ 7.63 (dd, J = 12.7, 1.6 Hz, 8H), 7.52 (s, 4H), 1.30 (s, 72H). ^{31}P NMR (162 MHz, DMSO-d6 and $CDCl_3$) δ 26.78. ^{13}C NMR (101 MHz, DMSO-d6 and $CDCl_3$) δ 150.6 (d, $J_{P\text{-}C}$ = 12.4 Hz), 134.2 (d, $J_{P\text{-}C}$ = 134.0 Hz), 125.4 (d, $J_{P\text{-}C}$ = 2.6 Hz), 125.3 (d, $J_{P\text{-}C}$ = 10.6 Hz), 35.0, 31.5. HRMS (ESI) calcd. For $[(C_{56}H_{84}O_2P_2)$+Na$]^+$ m/z 874.5839, found 874.5848.



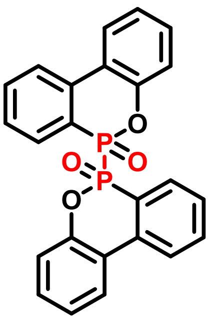
1,1,2,2-tetra(naphthalen-1-yl)diphosphane 1,2-dioxide (2g) Light yellow solid.M.P.:188.2-189.8 °C. 0.1082 g, 72% yield. ^{1}H NMR (400 MHz, DMSO-d6) δ 8.60 (d, J = 4.7 Hz, 4H), 8.21 (dd, J = 14.7, 6.6 Hz, 4H), 8.11 (d, J = 7.8 Hz, 4H), 7.96 (s, 4H), 7.64 (s, 4H), 7.49 (d, J = 3.1 Hz, 8H). ^{31}P NMR (162 MHz, DMSO-d6) δ 24.18. ^{13}C NMR (101 MHz, DMSO-d6) δ 133.7 (d, $J_{P\text{-}C}$ = 10.2 Hz), 133.1, 133.1, 133.0, 132.7 (d, $J_{P\text{-}C}$ = 10.9 Hz), 131.7 (d, $J_{P\text{-}C}$ = 131.0 Hz), 129.3, 127.0 (d, $J_{P\text{-}C}$ = 67.1 Hz), 126.9 (d, $J_{P\text{-}C}$ = 4.8 Hz), 125.4 (d, $J_{P\text{-}C}$ = 13.8 Hz). HRMS (ESI) calcd. For $[(C_{40}H_{28}O_2P_2)$+Na$]^+$m/z 625.1457, found 625.1458.



1,1,2,2-tetra(naphthalen-2-yl)diphosphane 1,2-dioxide (2h) Light yellow solid. M.P.: 164.2-169.3 °C. 0.1278 g, 80% yield. ^{1}H NMR (400 MHz, DMSO-d6) δ 8.47 (d, J = 13.8 Hz, 4H), 8.07 (d, J = 7.5 Hz, 4H), 8.01-7.91 (m, 8H), 7.81 (t, J = 9.2 Hz, 4H), 7.59 (dt, J = 13.3, 6.6 Hz, 8H). ^{31}P NMR (162 MHz, DMSO-d6) δ 23.44. ^{13}C NMR (101 MHz, DMSO-d6) δ 134.5 (d, $J_{P\text{-}C}$ = 2.2 Hz), 133.5, 132.7, 132.6, 132.3 (d, $J_{P\text{-}C}$ = 32.1 Hz), 129.3, 128.6 (d, $J_{P\text{-}C}$ = 12.3 Hz), 128.5, 127.8 (d, $J_{P\text{-}C}$ = 79.2 Hz), 127.1 (d, $J_{P\text{-}C}$ = 10.7 Hz). HRMS (ESI) calcd. For [($C_{40}H_{28}O_2P_2$)+H]$^+$ m/z 603.1637, found 603.1638.

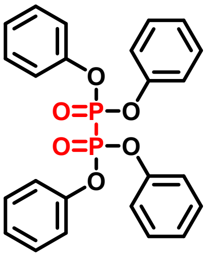


1,1,2,2-tetra([1,1'-biphenyl]-4-yl)diphosphane 1,2-dioxide (2i) White solid. M.p.: 258.1-259.3 °C. 78.9 mg, 89% yield. ^{1}H NMR (400 MHz, DMSO-d6 and $CDCl_3$) δ 7.88 – 7.80 (m, 9H), 7.79 – 7.72 (m, 7H), 7.68 (dd, J = 12.5, 7.4 Hz, 8H), 7.47 (dd, J = 14.6, 7.3 Hz, 8H), 7.38 (t, J = 7.3 Hz, 4H).^{31}P NMR (162 MHz, DMSO-d6 and $CDCl_3$) δ 23.42 (s), 18.09 (s). ^{13}C NMR (101 MHz, DMSO-d6 and $CDCl_3$) δ 143.6 (d, $J_{P\text{-}C}$ = 2.5 Hz), 139.7, 134.2 (d, $J_{P\text{-}C}$ = 136.4 Hz), 132.1 (d, $J_{P\text{-}C}$ = 10.3 Hz), 131.4 (d, $J_{P\text{-}C}$ = 11.8 Hz), 129.5, 129.5, 128.6, 127.7 (d, $J_{P\text{-}C}$ = 12.7 Hz), 127.5, 127.4, 127.2 (d, $J_{P\text{-}C}$ = 12.9 Hz). HRMS (ESI) calcd. For [($C_{48}H_{36}O_2P_2$)+H]$^+$ *m/z* 707.2263, found 707.2272.

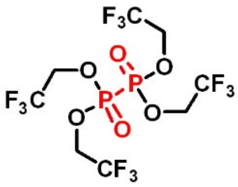


[6,6'-bidibenzo[c,e][1,2]oxaphosphinine] 6,6'-dioxide (2j) Yellow solid. M.P.: 207.6-208.1°C. 67.1mg, 62% yield. ^{1}H NMR (400 MHz, DMSO-d6) δ 8.19 - 8.11 (m, 2H), 7.78 (ddd, J = 23.9, 15.3, 8.0 Hz, 5H), 7.56 (ddd, J = 18.9, 11.4, 5.1 Hz, 4H), 7.48 – 7.41 (m, 2H), 7.35-7.23 (m, 3H). ^{31}P NMR (162 MHz, DMSO-d6) δ 5.98. ^{13}C NMR (101 MHz, DMSO-d6) δ 148.2 (d, $J_{P\text{-}C}$ = 7.0 Hz), 133.9 (d, $J_{P\text{-}C}$ = 6.7 Hz), 131.0 (d, $J_{P\text{-}C}$ = 2.2 Hz), 128.8, 127.2 (d, $J_{P\text{-}C}$ = 9.2 Hz), 126.7 (d, $J_{P\text{-}C}$ =

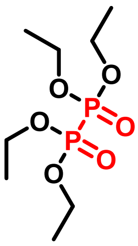
14.6 Hz), 125.1, 124.0, 122.7, 122.6, 121.1 (d, $J_{P\text{-}C}$ = 11.7 Hz), 118.4 (d, $J_{P\text{-}C}$ = 6.0 Hz). HRMS (ESI) calcd. For $[(C_{24}H_{16}O_4P_2)+H]^+$ m/z 431.0597, found 431.0603.



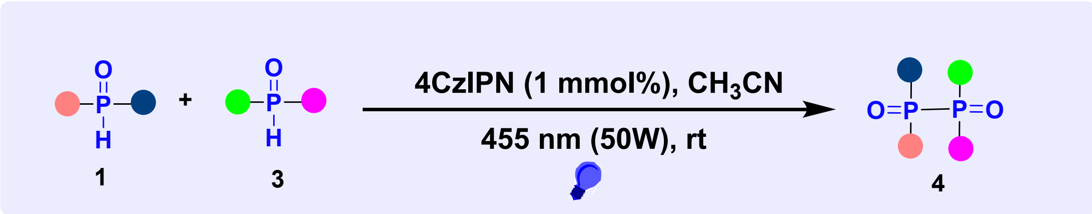
tetraphenyl hypodiphosphate (2k). Yellowish-brown liquid, 71.8 mg, 62% yield. ^{1}H NMR (400 MHz, DMSO-d6) δ 7.76 (dd, J = 15.7, 8.6 Hz, 1H), 7.46 (t, J = 7.8 Hz, 2H), 7.29 (t, J = 8.3 Hz, 3H), 7.22 (t, J = 7.8 Hz, 5H), 7.13 (d, J = 8.0 Hz, 5H), 6.96 (t, J = 7.2 Hz, 3H), 6.83 (d, J = 8.6 Hz, 1H). ^{31}P NMR (162 MHz, DMSO-d6) δ -11.60, -17.25 (Note: the torsional isomerization may lead to the formation of two peaks). ^{13}C NMR (101 MHz, DMSO-d6) δ 129.3, 129.2 (d, $J_{P\text{-}C}$ = 552.5 Hz), 126.6 (d, $J_{P\text{-}C}$ = 844.3 Hz), 120.37 (t, $J_{P\text{-}C}$ = 4.9 Hz). HRMS (ESI) calcd. For $C_{24}H_{20}O_6P_2$ m/z 466.0735, found 466.0728.



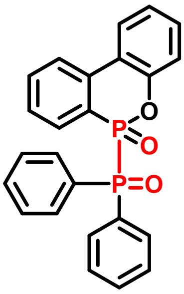
Tetrakis(2,2,2-trifluoroethyl) hypodiphosphate (2l). Yellow liquid, 93.6 mg, 76% yield. ^{1}H NMR (400 MHz, DMSO-d6) δ 4.54 – 3.80 (m, 8H). ^{31}P NMR (162 MHz, DMSO-d6) δ -3.15. ^{19}F NMR (376 MHz, DMSO-d6) δ -74.00. ^{13}C NMR (101 MHz, DMSO-d6) δ 124.9 (qd, $J_{P\text{-}C}$= 277.9, $J_{F\text{-}C}$=10.5 Hz), 62.3 (qd, $J_{F\text{-}C}$= 34.5, $J_{P\text{-}C}$=4.6 Hz). HRMS (ESI) calcd. For $[(C_8H_8F_{12}O_6P_2)+Na]^+$ m/z 512.9497, found 512.9498.



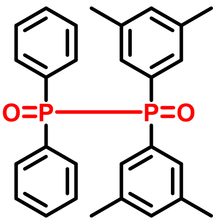
Tetraethyl hypodiphosphate (2m). Pale yellow liquid, 31.8 mg, 46% yield. ^{1}H NMR (400 MHz, DMSO-d6) δ 3.67 – 3.59 (m, 8H), 1.08 (t, J = 7.1 Hz, 12H). ^{31}P NMR (162 MHz, DMSO-d6) δ -0.64 (s). ^{13}C NMR (101 MHz, DMSO-d6) δ 59.6 (d, $J_{P\text{-}C}$ = 5.7 Hz), 17.1 (d, $J_{P\text{-}C}$ = 7.1 Hz). HRMS (ESI) calcd. For $[(C_8H_{20}O_6P_2)+Na]^+$ m/z 297.0627, found 297.0624.



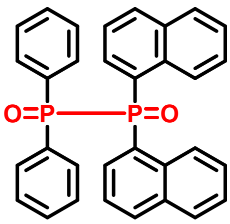
In a 10 mL Schlenk tube equipped with a magnetic stir bar, P(O)H compound **1** (0.5 mmol), **3** (0.5 mmol), and 4CzIPN (7.8 mg, 0.01 mmol) were placed. The system was filled with acetonitrile (2.0 mL). After sealing, the reaction mixture was irradiated with 50 W blue LEDs at room temperature for 24 - 120 h. The product **4** was obtained by filtration.



6-(diphenylphosphoryl)dibenzo[c,e][1,2]oxaphosphinine 6-oxide (4a) Yellow solid, M.P.: 137.5.6-138.2 °C. 153.4 mg, 74% yield. ^{1}H NMR (400 MHz, DMSO-d6) δ 7.73 (m, 8H), 7.55 – 7.45 (m, 10H). ^{31}P NMR (162 MHz, DMSO-d6) δ 23.42, 5.92. ^{13}C NMR (101 MHz, DMSO-d6) δ 150.4 (d, $J_{P\text{-}C}$= 6.9 Hz), 136.1, 134.7, 133.1 (d, $J_{P\text{-}C}$ = 2.0 Hz), 131.9 (d, $J_{P\text{-}C}$ = 2.7 Hz), 131.4, 131.3, 130.9 , 129.3 (d, $J_{P\text{-}C}$ = 9.3 Hz), 129.0, 128.9, 126.1, 124.9, 124.7, 123.2 (d, $J_{P\text{-}C}$ = 11.7 Hz), 120.5 (d, $J_{P\text{-}C}$ = 6.0 Hz). HRMS (ESI) calcd. For $[(C_{24}H_{18}O_3P_2)\text{-}H]^-$ m/z 415.0658, found 415.0655.

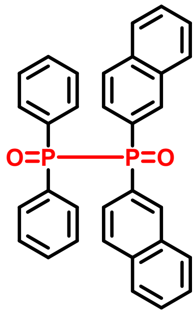


1,1-bis(3,5-dimethylphenyl)-2,2-diphenyldiphosphane 1,2-dioxide (4b) White solid, M.P.: 156.7-157.0 °C.191.5 mg, 84% yield. ^{1}H NMR (400 MHz, DMSO-d6) δ 7.76 - 7.70 (m, 4H), 7.43 (d, J = 7.1 Hz, 2H), 7.40 (dd, J = 7.5, 2.9 Hz, 4H), 7.33 (d, J = 12.3 Hz, 4H), 7.05 (s, 2H), 2.26 (s, 12H). ^{31}P NMR (162 MHz, DMSO-d6) δ 25.80, 24.66. ^{13}C NMR (101 MHz, DMSO-d6) δ 138.0, 137.8, 135.4 (d, $J_{P\text{-}C}$ = 132.8 Hz), 133.2, 131.8, 131.4 (d, $J_{P\text{-}C}$ = 9.6 Hz), 128.9 (d, $J_{P\text{-}C}$ = 23.4 Hz), 128.9, 21.3. HRMS (ESI) calcd. For $[(C_{28}H_{28}O_2P_2)+H]^+$ m/z 459.1638, found 459.1630.

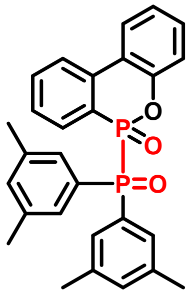


1,1-di(naphthalen-1-yl)-2,2-diphenyldiphosphane 1,2-dioxide (4c) Light yellow solid, M.P.: 143.6-144.3 °C. 225.3 mg, 90% yield. ^{1}H NMR (400 MHz, DMSO-d6) δ 8.65 – 8.54 (m, 2H), 8.21 (dd, J = 14.7, 7.4 Hz, 2H), 8.11 (d, J = 8.2 Hz, 2H), 7.98 – 7.93 (m, 2H), 7.78 – 7.71 (m, 6H), 7.66 – 7.59 (m, 2H), 7.51 – 7.45 (m, 8H). ^{31}P NMR (162 MHz, DMSO-d6) δ 24.17, 23.44. ^{13}C

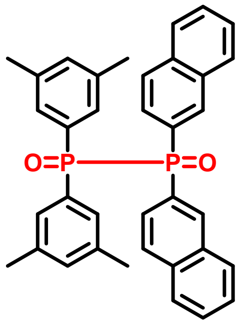
NMR (101 MHz, DMSO-d6) δ 135.4 (d, $J_{P\text{-}C}$ = 134.6 Hz), 133.7 (d, $J_{P\text{-}C}$ = 10.3 Hz), 133.1 (d, $J_{P\text{-}C}$ = 2.8 Hz), 133.0, 132.7 (d, $J_{P\text{-}C}$ = 10.8 Hz), 131.9 (d, $J_{P\text{-}C}$ = 2.4 Hz), 131.7 (d, $J_{P\text{-}C}$ = 131.0 Hz), 131.4 (d, $J_{P\text{-}C}$ = 10.0 Hz), 130.2 (d, $J_{P\text{-}C}$ = 237.7 Hz), 130.1 (d, $J_{P\text{-}C}$ = 260.2 Hz), 129.3, 127.0 (d, $J_{P\text{-}C}$ = 66.7 Hz), 126.9 (d, $J_{P\text{-}C}$ = 4.6 Hz), 125.4 (d, $J_{P\text{-}C}$ = 13.8 Hz).HRMS (ESI) calcd. For $[(C_{32}H_{25}O_2P_2)+H]^+$ *m/z* 503.1325, found 503.1335.



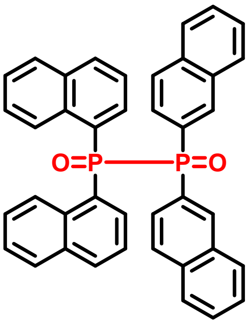
1,1-di(naphthalen-2-yl)-2,2-diphenyldiphosphane 1,2-dioxide (4d) Light yellow solid. M.P.:145.3-146.2 °C. 0.2026 g, 81% yield. ^{1}H NMR (400 MHz, DMSO-d6) δ 8.63-8.54 (m, 2H), 8.21 (dd, *J* = 14.7, 7.4 Hz, 2H), 8.11 (d, *J* = 8.2 Hz, 2H), 7.95 (d, *J* = 7.5 Hz, 2H), 7.78 - 7.71 (m, 6H), 7.67 - 7.59 (m, 2H), 7.50 - 7.45 (m, 8H). ^{31}P NMR (162 MHz, DMSO-d6) δ 23.47 (d, *J* = 14.2 Hz). ^{13}C NMR (101 MHz, DMSO-d6) δ 135.4 (d, $J_{P\text{-}C}$ = 134.7 Hz), 134.5 (d, $J_{P\text{-}C}$ = 2.2 Hz), 133.4, 132.7, 132.6, 132.3 (d, $J_{P\text{-}C}$ = 36.0 Hz), 131.9 (d, $J_{P\text{-}C}$ = 2.5 Hz), 130.2 (d, $J_{P\text{-}C}$ = 238.3 Hz), 130.1 (d, $J_{P\text{-}C}$ = 260.7 Hz), 129.3, 128.6 (d, $J_{P\text{-}C}$ = 12.3 Hz), 128.5, 127.8 (d, $J_{P\text{-}C}$ = 79.8 Hz), 127.1 (d, $J_{P\text{-}C}$ = 10.6 Hz). HRMS (ESI) calcd. For $[(C_{32}H_{24}O_2P_2)+Na]^+$ m/z 525.1144, found 525.1143.



6-(bis(3,5-dimethylphenyl)phosphoryl)dibenzo[c,e][1,2]oxaphosphinine 6-oxide (4e) White solid, M.P.: 176.6-177.7 °C. 158.6 mg, 66% yield. ^{1}H NMR (400 MHz, DMSO-d6) δ 8.10 (d, *J* = 7.1 Hz, 2H), 7.81 (s, 1H), 7.72 (t, *J* = 7.4 Hz, 1H), 7.54 (s, 1H), 7.45 - 7.20 (m, 7H), 7.11 (s, 2H), 2.28 (s, 12H). ^{31}P NMR (162 MHz, DMSO-d6) δ 24.37, 5.68 ^{13}C NMR (101 MHz, DMSO-d6) δ 150.5, 138.0, 137.9, 136.0, 134.7, 133.2, 132.9, 130.7, 129.3, 129.0, 128.9 (d, $J_{P\text{-}C}$ = 9.5 Hz), 128.6 (d, $J_{P\text{-}C}$ = 11.9 Hz), 126.0, 124.7, 123.3 (d, $J_{P\text{-}C}$ = 6.3 Hz), 120.5 (d, $J_{P\text{-}C}$ = 7.4 Hz), 21.3. HRMS (ESI) calcd. For $[(C_{28}H_{25}O_3P_2)-H]^-$ *m/z* 471.1284, found 471.1273.



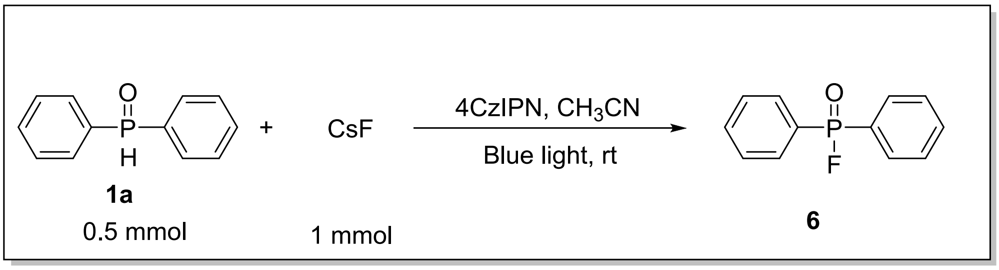
1,1-bis(3,5-dimethylphenyl)-2,2-di(naphthalen-2-yl)diphosphane 1,2-dioxide (4f) Yellowish-brown solid, M.P.: 147.6-148.4 °C.153.8 mg, 86% yield. ^{1}H NMR (400 MHz, DMSO-d6) δ 8.46 (d, *J* = 13.7 Hz, 2H), 8.04 (d, *J* = 7.6 Hz, 2H), 7.99 – 7.90 (m, 4H), 7.80 (t, *J* = 9.2 Hz, 2H), 7.65 – 7.50 (m, 4H), 7.33 (d, J = 12.2 Hz, 4H), 7.10 (s, 1H), 2.25 (s, 2H). ^{31}P NMR (162 MHz, DMSO-d6) δ 23.97, 23.07. ^{13}C NMR (101 MHz, DMSO-d6) δ 137.9 (d, J_{P-C} = 13.2 Hz), 135.5 (d, J_{P-C} = 133.7 Hz), 134.4 (d, J_{P-C} = 2.1 Hz), 133.7, 133.2 (d, J_{P-C} = 2.3 Hz), 132.6 (d, J_{P-C} = 2.0 Hz), 132.5 (d, J_{P-C} = 21.2 Hz), 129.3, 129.0 (d, J_{P-C} = 9.8 Hz), 128.5 (d, J_{P-C} = 12.4 Hz), 128.4, 128.1, 127.3, 127.2 (d, J_{P-C} = 10.7 Hz), 21.3. HRMS (ESI) calcd. For $[(C_{36}H_{32}O_2P_2)+H]^+$ m/z 559.1951, found 559.1953.



1,1-di(naphthalen-1-yl)-2,2-di(naphthalen-2-yl)diphosphane 1,2-dioxide (4g) yellowish-brown solid, M.P.: 153.8.6-154.2 °C. 196.7 mg, 65% yield. ^{1}H NMR (400 MHz, DMSO-d6) δ 8.62 (d, J = 5.1 Hz, 1H), 8.49 (d, J = 13.7 Hz, 2H), 8.34 (s, 1H), 8.22 (dd, J = 15.2, 6.4 Hz, 2H), 8.13 – 8.01 (m, 5H), 7.94 (dd, J = 17.1, 7.8 Hz, 5H), 7.86 – 7.77 (m, 2H), 7.58 (dd, J = 13.7, 7.0 Hz, 8H), 7.47 (d, J = 7.2 Hz, 2H). ^{31}P NMR (162 MHz, DMSO-d6) δ 23.08, 17.13. ^{13}C NMR (101 MHz, DMSO-d6) δ 134.5 (d, J_{P-C} = 2.1 Hz), 133.9 (d, J_{P-C} = 2.4 Hz), 133.8, 133.7, 133.1, 133.0 (d, J_{P-C} = 2.7 Hz), 132.6 (d, J_{P-C} = 8.1 Hz), 132.4 (d, J_{P-C} = 11.4 Hz), 130.5 (d, J_{P-C} = 160.9 Hz), 129.3, 128.6 (d, J_{P-C} = 12.2 Hz), 128.4, 127.7 (d, J_{P-C} = 83.3 Hz), 127.2 (d, J_{P-C} = 2.9 Hz), 127.1, 127.0 (d, J_{P-C} = 4.7 Hz), 126.6, 125.8 (d, J_{P-C} = 14.3 Hz), 125.4 (d, J_{P-C} = 13.8 Hz), 125.2 (d, J_{P-C} = 7.5 Hz). HRMS (ESI) calcd. For $[(C_{40}H_{28}O_2P_2)+H]^+$ m/z 603.1638, found 603.1638.

4. Mechanistic investigation

4.1 Control experiment



A Schlenk reaction tube equipped with a magnetic stir bar was charged with diphenylphosphine oxide (101 mg, 0.5 mmol), cesium fluoride (152 mg, 1 mmol), and 4CzIPN (3.9 mg, 0.005 mmol, 1 mol%). Acetonitrile (2.0 mL) was then added. The reaction mixture was irradiated at room temperature with a 50 W blue LEDs source for 72 h. No solid precipitated during the reaction, and diphenylphosphine oxide was observed. TLC analysis indicated the formation of a new product. After removal of the solvent under reduced pressure, the residue was analyzed by GC-MS, confirming the formation of the target compound.

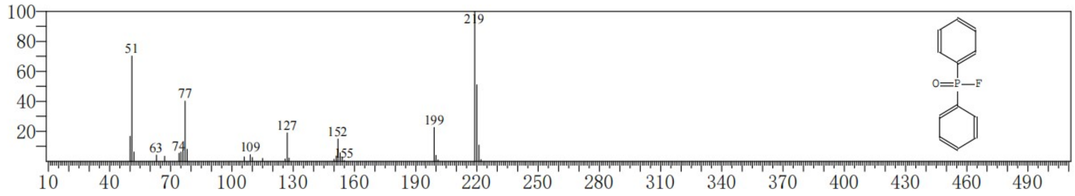
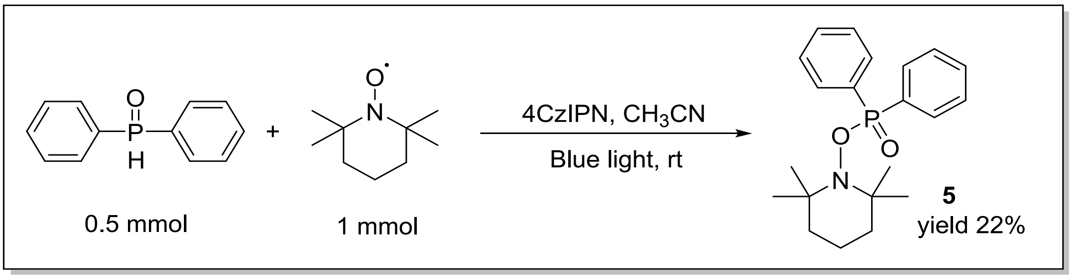


Figure S2. GC-MS spectrum of **6**

4.2 TEMPO radical-trapping experiments



A dry Schlenk tube was charged with diphenylphosphine oxide (101 mg, 0.5 mmol), TEMPO (156 mg, 1 mmol), and photocatalyst 4CzIPN (3.9 mg, 0.005 mmol, 1 mol%). Acetonitrile (2 mL) was added as the solvent. The reaction mixture was stirred and irradiated at room temperature with a 50 W blue LED for 24 h. After completion, the mixture was purified by column chromatography on silica gel. A gradient elution was performed using petroleum ether/ethyl acetate (v/v = 15:1, 10:1, 8:1). The target product, corresponding to the TEMPO - adduct **5**, was eluted at 8:1, collected, and concentrated to afford the desired compound in 22% isolated yield.

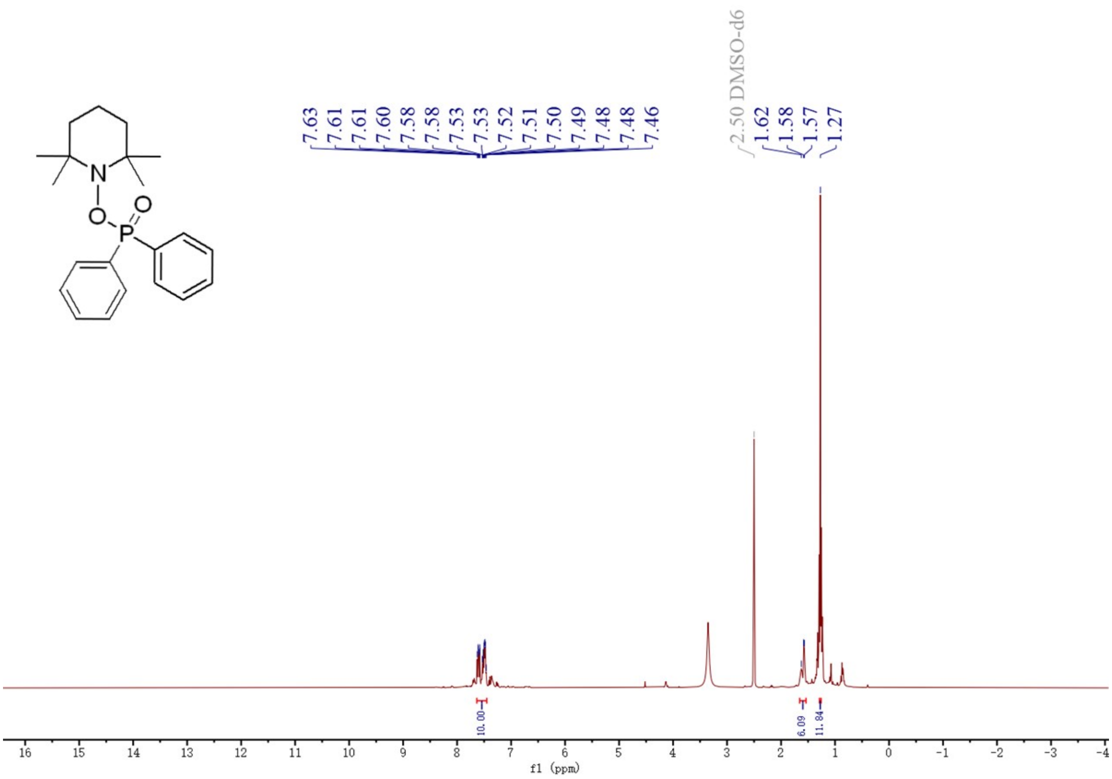


Figure S3. ^{1}HNMR (400 MHz) Spectrum of 5 in DMSO-d6

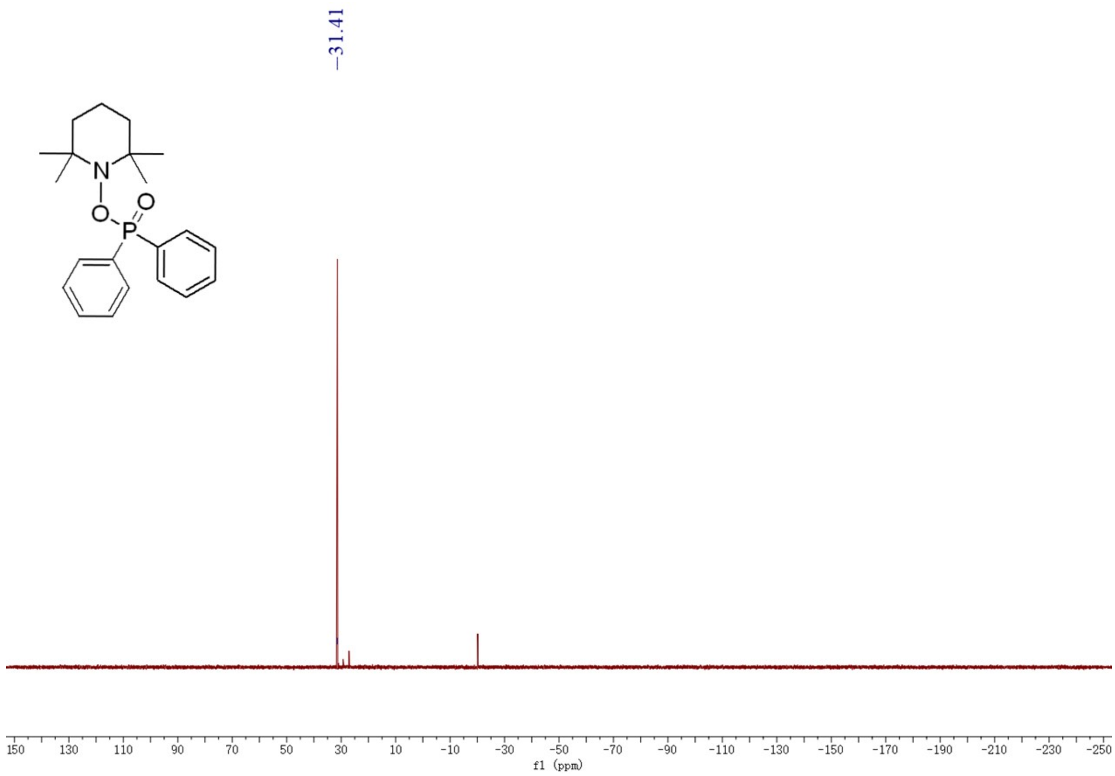


Figure S4. [31]P NMR (162 MHz) Spectrum of 6 in DMSO-d6

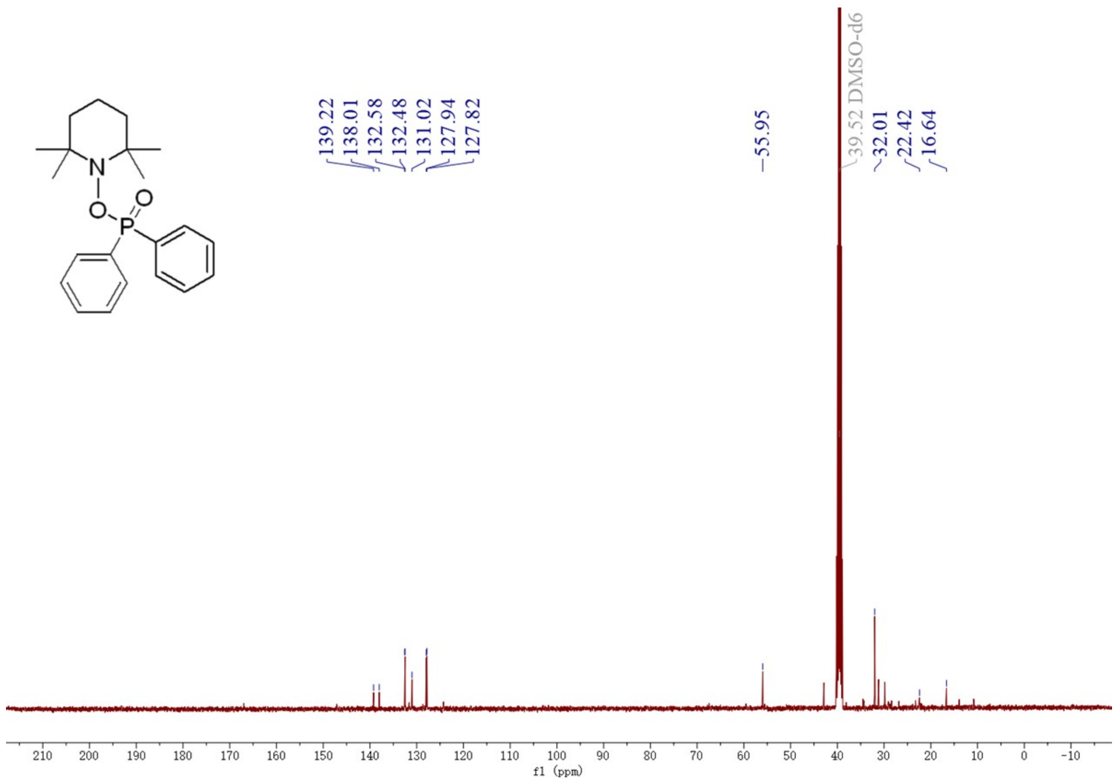


Figure S5. [13]C NMR (101 MHz) Spectrum of 6 in DMSO-d6

4.3 Stern - Volmer experiments

A 0.025 mmol/L solution of 4CzIPN in acetonitrile and a 2 mmol/L acetonitrile solution of quencher **1a** were prepared using a volumetric flask. During the experiment, freshly prepared

0.025 mmol/L 4CzIPN acetonitrile solution was sequentially added to quartz cuvettes containing different volumes (20, 40, 60, 80, 100 μL) of quencher **1a** solution. Fluorescence spectroscopy measurements were conducted at room temperature. Fluorescence emission spectra in the range of 450 - 750 nm were detected upon excitation at a wavelength of 420 nm. The effect of varying concentrations of quencher 1a on the fluorescence intensity of the system was investigated.

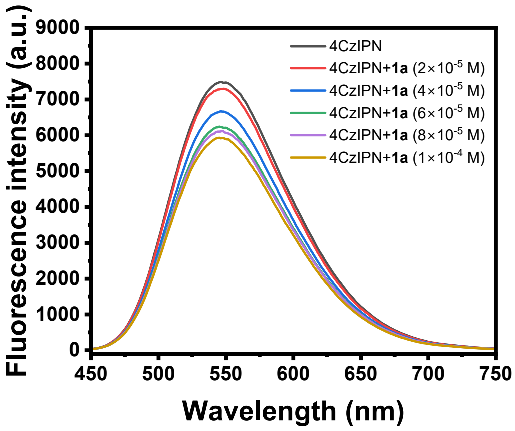


Figure S6. Stern - Volmer curves

4.4 EPR experiments

Diphenylphosphine oxide **1a** (202 mg, 0.5 mmol) and 4CzIPN (3.9 mg, 1 mmol%) were placed in a photochemical reaction tube. Acetonitrile (2 mL) was added as the solvent, and then the mixture was irradiated for 6 hours in a photochemical reactor until solid formation. A radical scavenger, DMPO (226 mg, 2 mmol), was added, and sampling was immediately performed using a capillary for electron paramagnetic resonance (EPR) testing. The results revealed distinct radical characteristic signals in the EPR spectrum, indicating that this signal may originate from the reactive intermediate radicals generated during the reaction process.

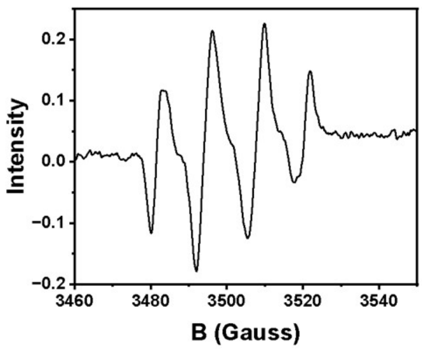


Figure S7. EPR curves

5. Recycling and kilogram-scale amplification reaction

5.1 Recycling experiments with a 500 mL beaker photoreactor

To a self - made 500 mL beaker photoreactor, **1a** (0.1 mol, 20.2 g) and photocatalyst 4CzIPN (0.1 mmol, 78.8 mg) were added. The reactants were dissolved in 100 mL of acetonitrile. A stir bar was added, and the reaction was allowed to proceed at room temperature for 48 h while being stirred on a stir plate. The resulting yellow mixture was filtered, washed with acetonitrile (50 mL), and dried to afford the white product **2a** in 97% yield. The filtrate, which contained the photocatalyst and acetonitrile, could be reused for four additional reaction cycles after supplementing it with 0.1 mol of **1a**. Following the same work - up procedure, the yields were 97%, 94%, 94%, and 94%, respectively. Repeating the same procedure over five runs yielded 2a with an overall yield of 95%, and the solvent recovery rate was 93%.

Table S2 Recovery of acetonitrile

Number of cycles	1	2	3	4	5
Initial volume (mL)	100	97	95	94	92
Volume of the filtrate (mL)	97	95	94	91	89

5.2 Kilogram-scale amplification experiment

A self - made 2000 mL beaker - type photoreactor was charged with **1a** (4.95 mol, 1 kg) and photocatalyst 4CzIPN (0.1 mmol, 3.9 g). The mixture was dissolved in 1000 mL of acetonitrile, and then a stir bar was added. The reaction mixture was stirred at room temperature for 240 hours. After completion of the reaction, the resulting yellow solid–liquid mixture was filtered, washed with acetonitrile, and dried to obtain the white product **2a** in 85% yield.

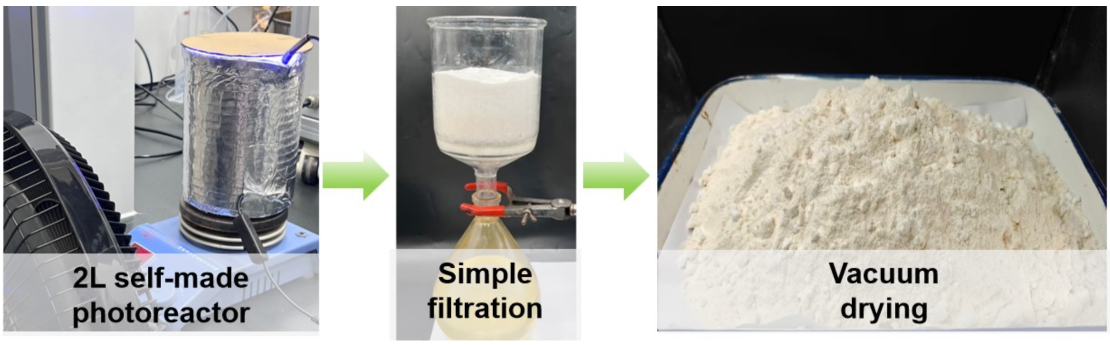


Figure S8. Kilogram-scale amplification of **1a**

6. Calculation of green chemistry metrics

To evaluate the green chemistry aspects of the developed reaction, we calculated the green chemistry metrics, including atom economy (AE), process mass intensity (PMI), E - factor, carbon efficiency (CE), reaction mass efficiency (RME), and EcoScale point.

Our work:

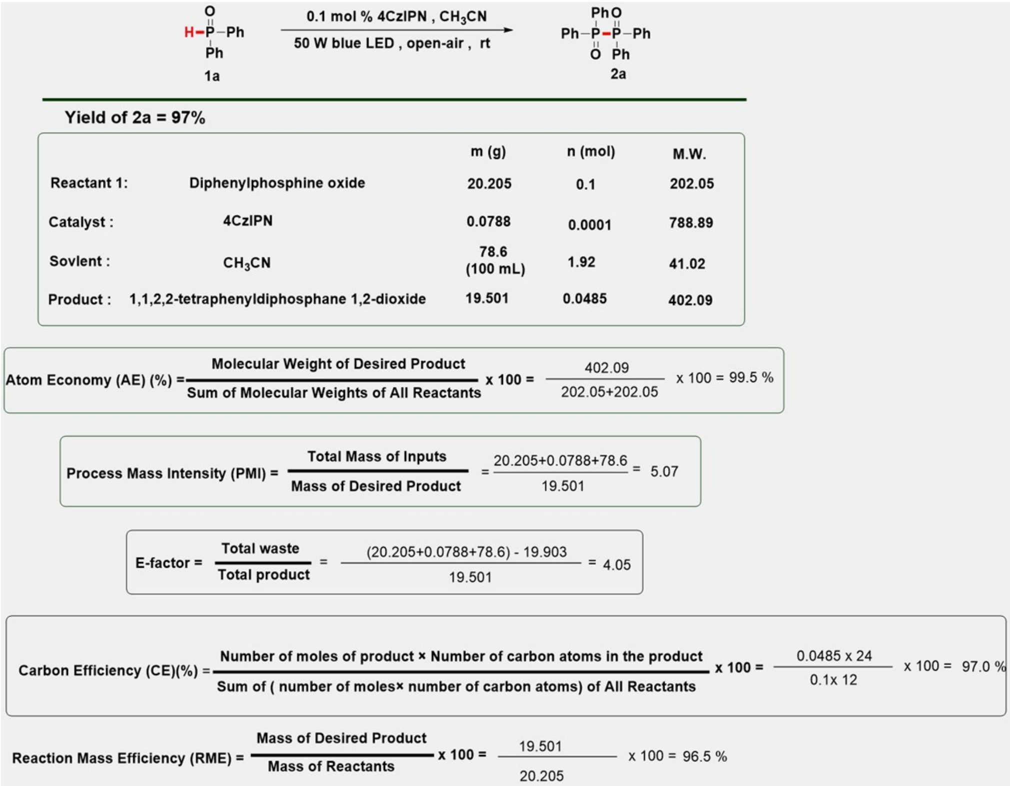


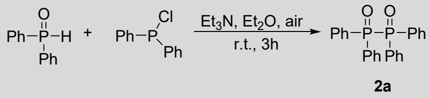
Figure S9. Calculation details of green chemistry metrics for **2a** (our work)

Table S3 The penalty points for our work according to EcoScale [a]

Parameters	Penalty
1 Yield: 97%	1.5
2 4CzIPN, CH_3CN	0
3 25°C, 48 h	1
4 Cooling	0
Recycling of CH_3CN	0
Filtration	0
Penalty points total:	2.5

[a] Ranking of reaction conditions : The reaction conditions used in the preparation of a high purity product is ranked on a scale from 0 to 100 using the following scores: > 75. excellent; >50, acceptable; and < 50, inadequate.

Other work: *J. Org. Chem.* 1966, **31**, 1206-1209.



Yield of 2a = 72%

		m (g)	n (mol)	M.W.
Reactant 1:	Diphenylphosphine oxide	10.890	0.0539	202.05
Reactant 2 :	Diphenylphosphinous chloride	11.859	0.0539	220.02
Reactant 3 :	Triethylamine	5.450	0.0539	101.12
Sovlent :	Et_2O	105.9 (150 mL)	1.429	74.07
Product :	1,1,2,2-tetraphenyldiphosphane 1,2-dioxide	15.604	0.0388	402.09

$$\text{Atom Economy (AE) (\%)} = \frac{\text{Molecular Weight of Desired Product}}{\text{Sum of Molecular Weights of All Reactants}} \times 100 = \frac{402.09}{202.05+220.02+5.45} \times 100 = 94.0\ \%$$

$$\text{Process Mass Intensity (PMI)} = \frac{\text{Total Mass of Inputs}}{\text{Mass of Desired Product}} = \frac{10.890+11.859+5.450+105.9}{15.604} = 8.59$$

$$\text{E-factor} = \frac{\text{Total waste}}{\text{Total product}} = \frac{(10.890+11.859+5.45+105.9) - 15.604}{15.604} = 7.59$$

$$\text{Carbon Efficiency (CE)(\%)} = \frac{\text{Number of moles of product} \times \text{Number of carbon atoms in the product}}{\text{Sum of (number of moles} \times \text{number of carbon atoms) of All Reactants}} \times 100 = \frac{0.0388 \times 24}{(0.0539 \times (12+12+6)} \times 100 = 58\%$$

$$\text{Reaction Mass Efficiency (RME)} = \frac{\text{Mass of Desired Product}}{\text{Mass of Reactants}} \times 100 = \frac{15.604}{28.199} \times 100 = 55.3\%$$

Figure S10. Calculation details of green chemistry metrics for **2a** (other work)

Table S4 The penalty points for our work according to EcoScale [a]

Parameters	Penalty
1 Yield: 72%	14
2 Diphenylphosphinous chloride (F, > $10)	8
Diphenylphosphine oxide	0
Et_3N （T, F）	10
3 Et_2O (T, F+）	15
4 25°C, 3 h	0
5 Filtration	0
Penalty points total:	47

[a] Ranking of reaction conditions : The reaction conditions used in the preparation of a high purity product is ranked on a scale from 0 to 100 using the following scores: > 75. excellent; >50, acceptable; and < 50, inadequate.

7. Preparation of flame-retardant epoxy resin with 2a

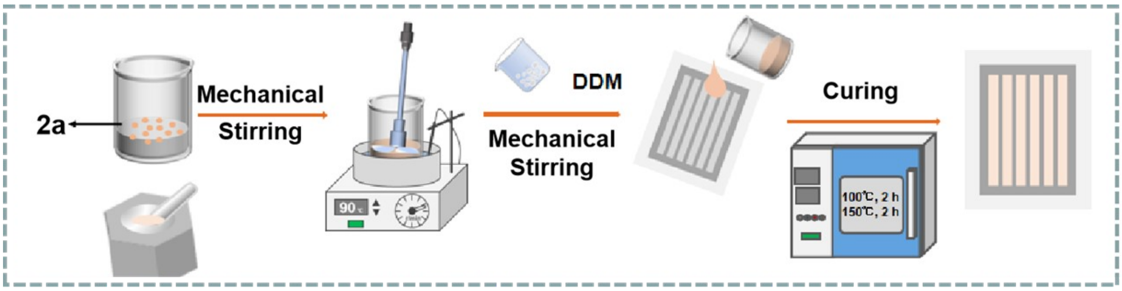


Figure S11. Preparation of flame-retardant epoxy resin with **2a**

First, a uniform mixture was obtained by mechanically stirring the flame retardant **2a** with DGEBA (E44) in an oil bath heated to 90 °C for 30 min. Subsequently, the curing agent DDM was added to the mixture while continuously mechanically stirring for 5 min, yielding a transparent blend. The resulting mixture was quickly transferred into preheated stainless - steel molds (with dimensions of 130 mm × 6.5 mm × 3.2 mm for limiting oxygen index tests, 130 mm × 13 mm × 3.2 mm for vertical burning tests, 75 mm × 10 mm × 2 mm for tensile performance tests, and 80 mm × 10 mm × 4 mm for unnotched impact performance tests). The molds were covered with film, secured, and placed in a forced - air oven for curing at 100 °C for 2 h, followed by post - curing at 150 °C for an additional 2 h to obtain the flame - retardant cured epoxy resin. The cured epoxy resins containing 1 wt%, 2 wt%, and 3 wt% of 2a are designated as EP/$2a_{1\%}$, EP/$2a_{2\%}$, and EP/$2a_{3\%}$, respectively. A reference sample of neat epoxy resin (Neat EP) without a flame retardant was prepared using the same procedure. The formulations and the LOI and UL-94 tests data of the cured epoxy resins are summarized in Table S5 and S6.

Table S5. Epoxy resin formulations

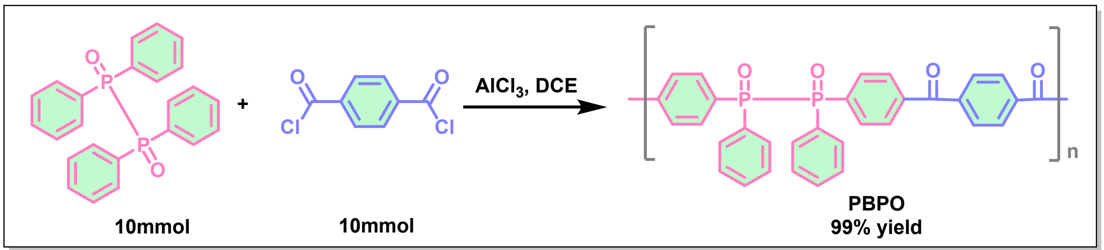
Samples	2a (g)	E44 (g)	DDM (g)
Neat EP	0	80	20
EP/$2a_{1\%}$	1	79.2	19.8
EP/$2a_{2\%}$	2	78.4	19.6
EP/$2a_{3\%}$	3	77.6	19.4

Table S6. The LOI and UL-94 tests data of EP and EP/2a samples

Samples	P-content (wt%)	LOI (%)	UL-94		Dropping (Yes/No)
			$t_1 + t_2$ (s)	Rating	
Neat EP	0	26.5	-	NR [a]	No
EP/$2a_{1\%}$	0.15	32.0	23	V-1	No
EP/$2a_{2\%}$	0.31	38.5	8	V-0	No
EP/$2a_{3\%}$	0.46	39.5	4	V-0	No

[a] NR means no rating.

8.Synthesis and characteristic data of polydiphosphine dioxide polymer PBPO



A three - necked flask was charged with $AlCl_3$ (0.05 mol, 6.5 g) under a nitrogen atmosphere. Then, dichloroethane (DCE, 20 mL) was added. The flask was placed in an ice bath at 0 °C. A mixture of N,N - dimethylformamide (DMF, 0.5 mL) and DCE (10 mL) was added dropwise to the flask until the solution became clear. The temperature of the cooling bath was then adjusted to −10 °C. Compound **2a** (11 mmol, 4.02 g) and terephthaloyl chloride (TPC, 10 mmol, 2.03 g) were added to the reaction mixture. The reaction was allowed to proceed at this low temperature for 1 h. Subsequently, the reaction mixture was warmed to 25 °C and stirred for 48 h. The reaction was quenched by the slow addition of methanol (30 mL), during which a small amount of white fumes evolved, and a white solid precipitated. The solid was collected by filtration and washed sequentially with dilute hydrochloric acid, formic acid, and water until the filtrate reached a neutral pH. The resulting solid was further washed with a mixture of DCM and methanol, dried, and ground into a white powder. The yield was 99%.

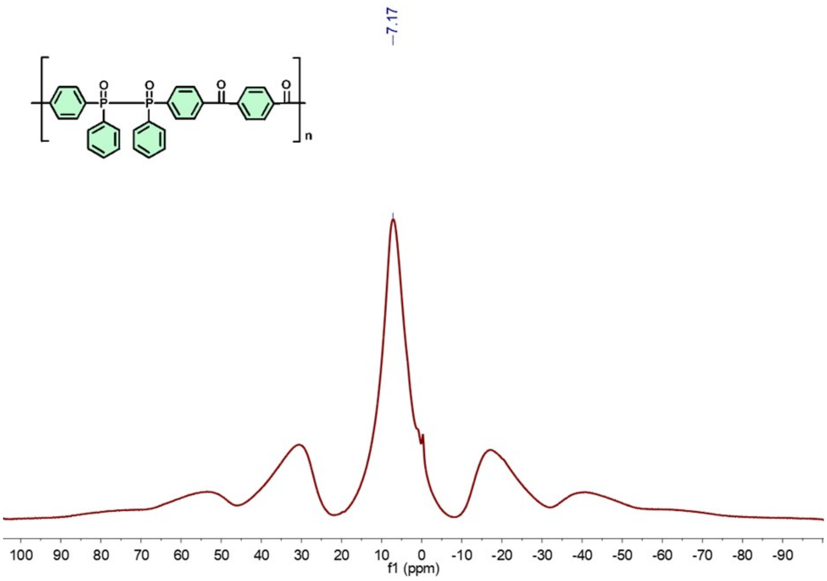


Figure S12. Solid-state ^{1}H NMR spectrum of **PBPO**

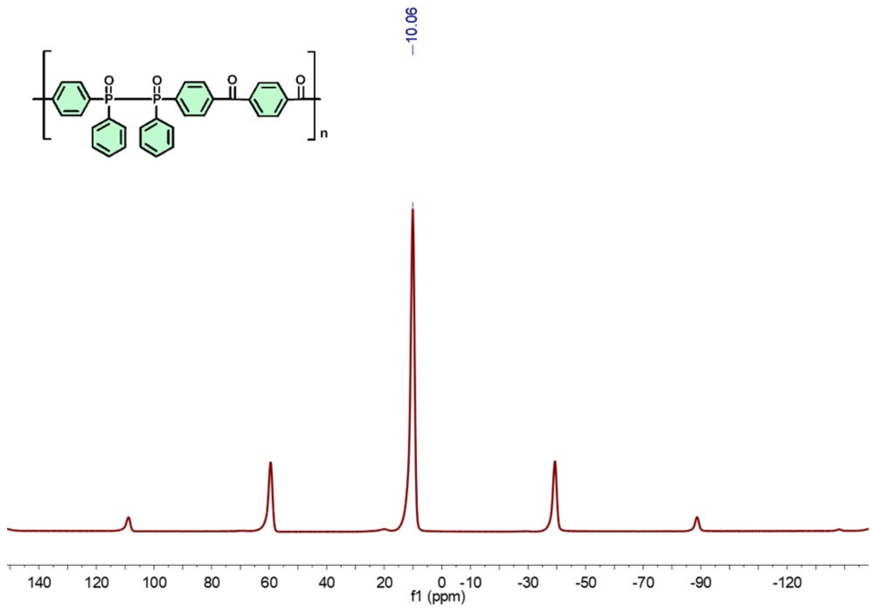


Figure S13. Solid-state ^{31}P NMR spectrum of **PBPO**

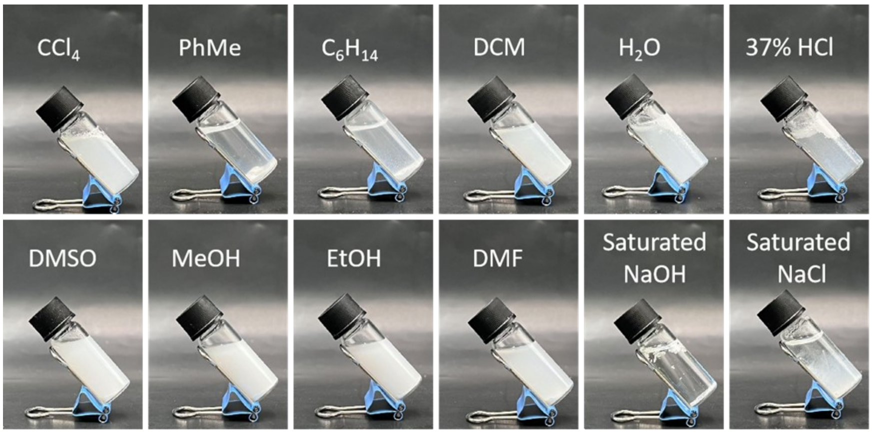


Figure S14. Solubility test of **PBPO**

9. Preparation for polyurethane foam

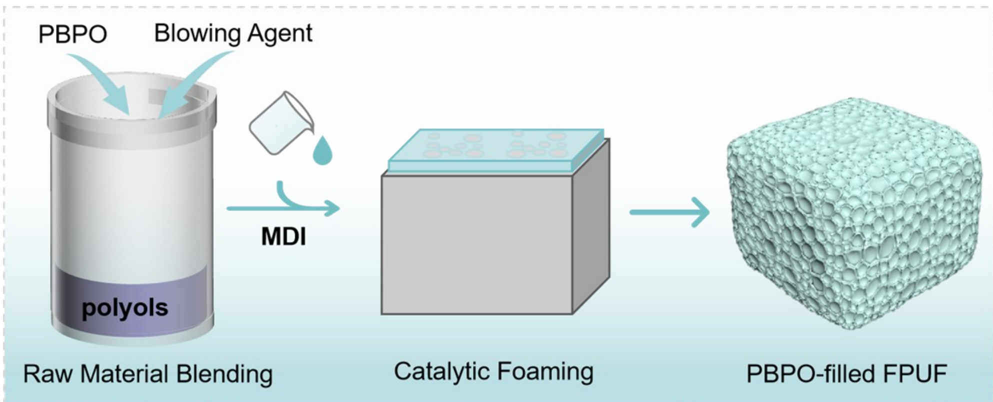


Figure S15. Preparation for polyurethane foam

The polyurethane foam was prepared via a one-step molding process, with its density controlled within the range of 60-70 kg·m^{-3} by adjusting the formulation to eliminate mechanical property fluctuations caused by density variations. Polyether polyol (DEP-330G), distilled water, surfactant (DC2525), triethanolamine (TEOA), catalysts (A1 and T12), and anti-aging agent (PBPO) were sequentially added to a plastic beaker and mixed at 3000 rpm for 3 minutes.

Under continuous stirring at 3000 rpm, modified 4,4'-diphenylmethane diisocyanate (MDI-2412) was then introduced into the mixture. Within 5 seconds after MDI addition, the resulting mixture was quickly poured into an open plastic mold. The amount of MDI was calculated based on the isocyanate index (NCO/OH ratio = 1.05). The foam was cured at 70 °C for 2 minutes. The specific foaming formulation is shown in the table S7.

Table S7. The formulations of polyurethane foam

Samples	PBPO (g)	330N (g)	H_2O (g)	DC-2525 (g)	TEOA (g)	A-1 (g)	T-12 (g)	MDI-2412 (g)	ρ (kg/m^3)
Neat FPUF	0	100	2	2	2	0.15	0.2	44.4	66
FPUF-5	5	100	2	2	2	0.15	0.2	44.4	62
FPUF-15	15	100	2	2	2	0.15	0.2	44.4	64

10. Mechanical test of pure-FPUF and FPUF/5PBPO

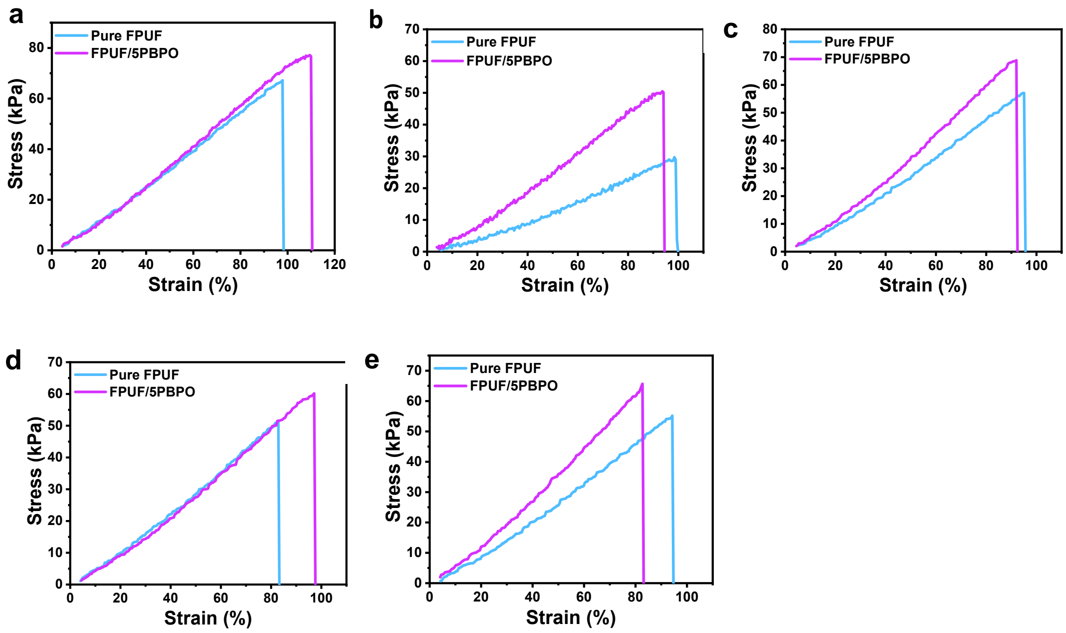


Figure S16. Tensile strength of pure fpuf and fpuf containing 5 phr antioxidant pbpo under various aging conditions. aging conditions: (a) UV aging, (b) thermal aging, (c) acid aging, (d) alkali aging, (e) salt aging.

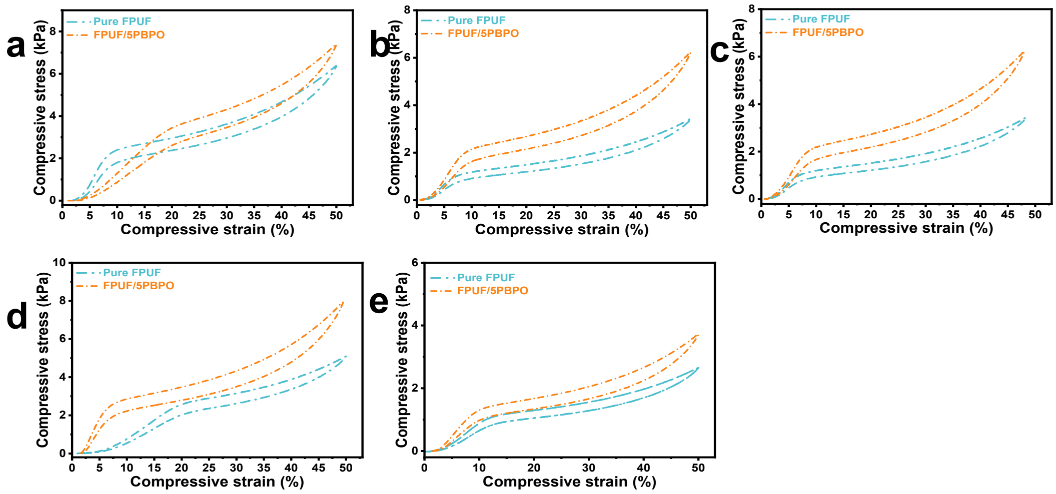
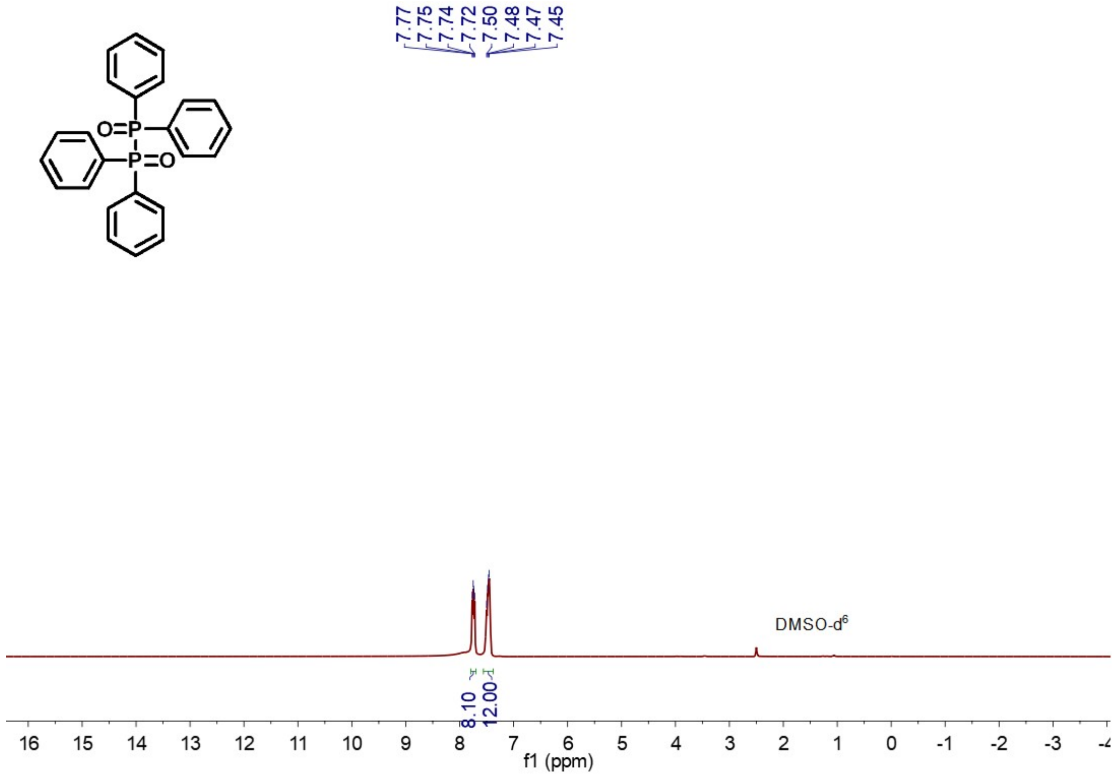


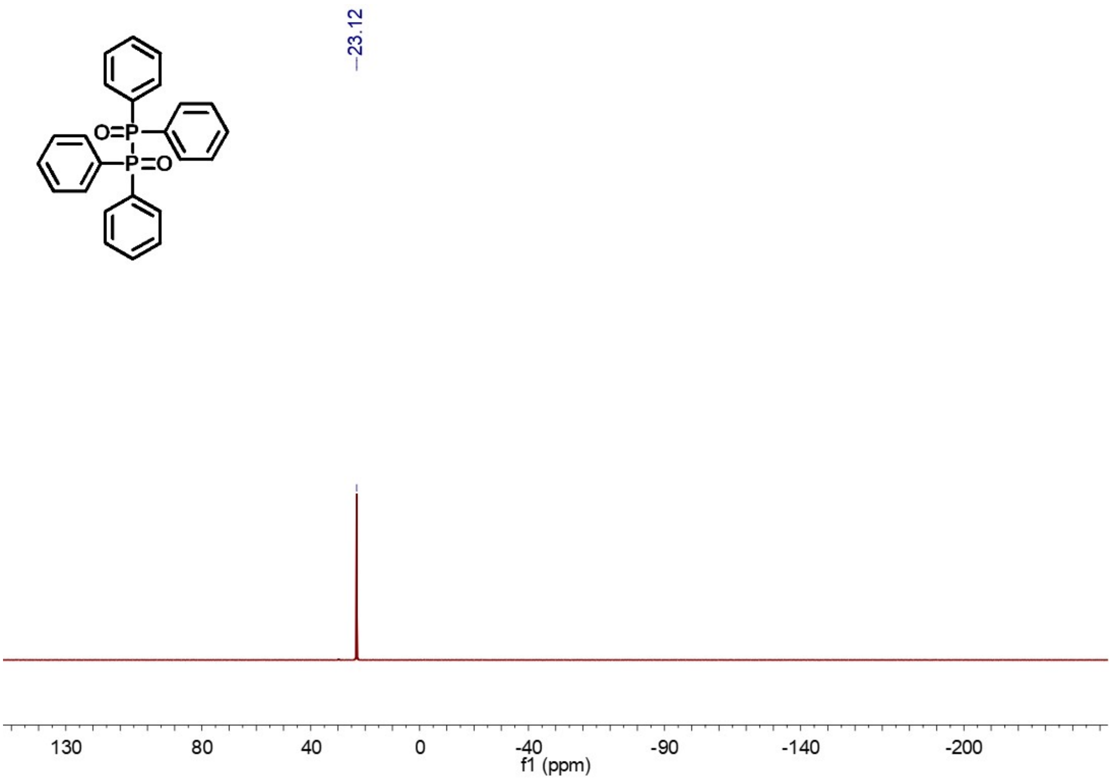
Figure S17. Compressive strength of pure fpuf and fpuf containing 5 phr antioxidant pbpo under various aging conditions. aging conditions: (a) UV aging, (b) thermal aging, (c) acid aging, (d) alkali aging, (e) salt aging.

11. Copies of NMR and HRMS spectra of compounds 2a-2m and 4a-4g

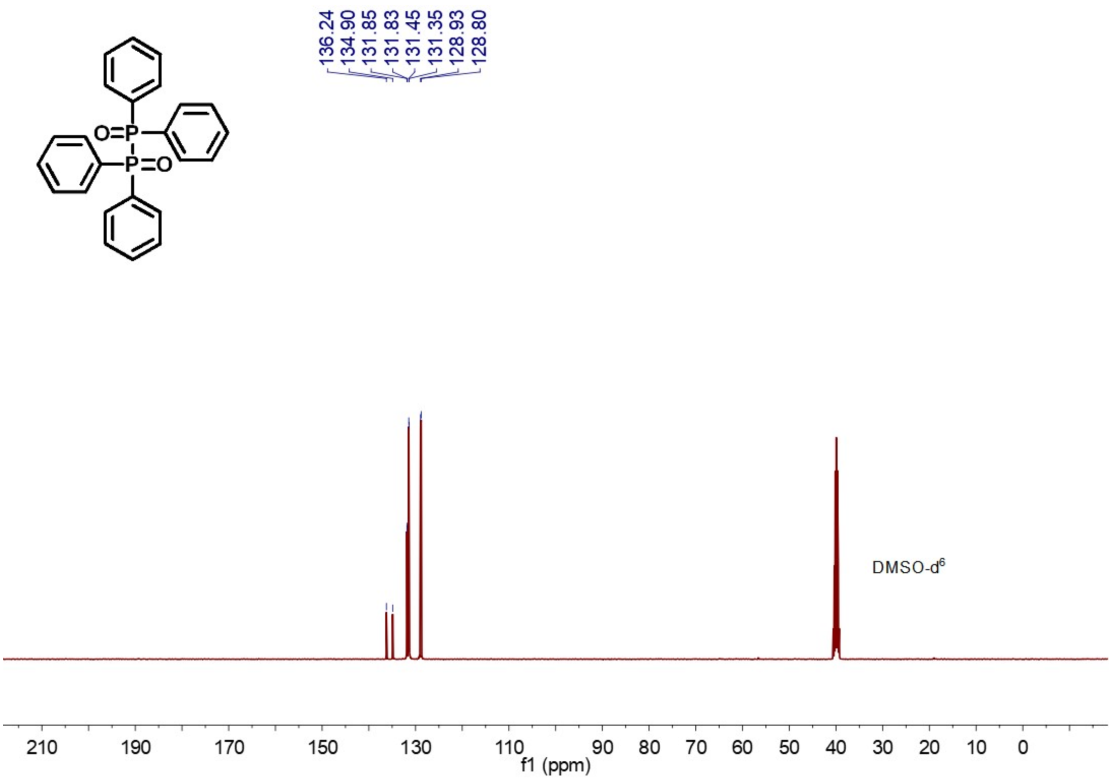
^{1}HNMR (400 MHz) Spectrum of 2a in DMSO-d^{6}



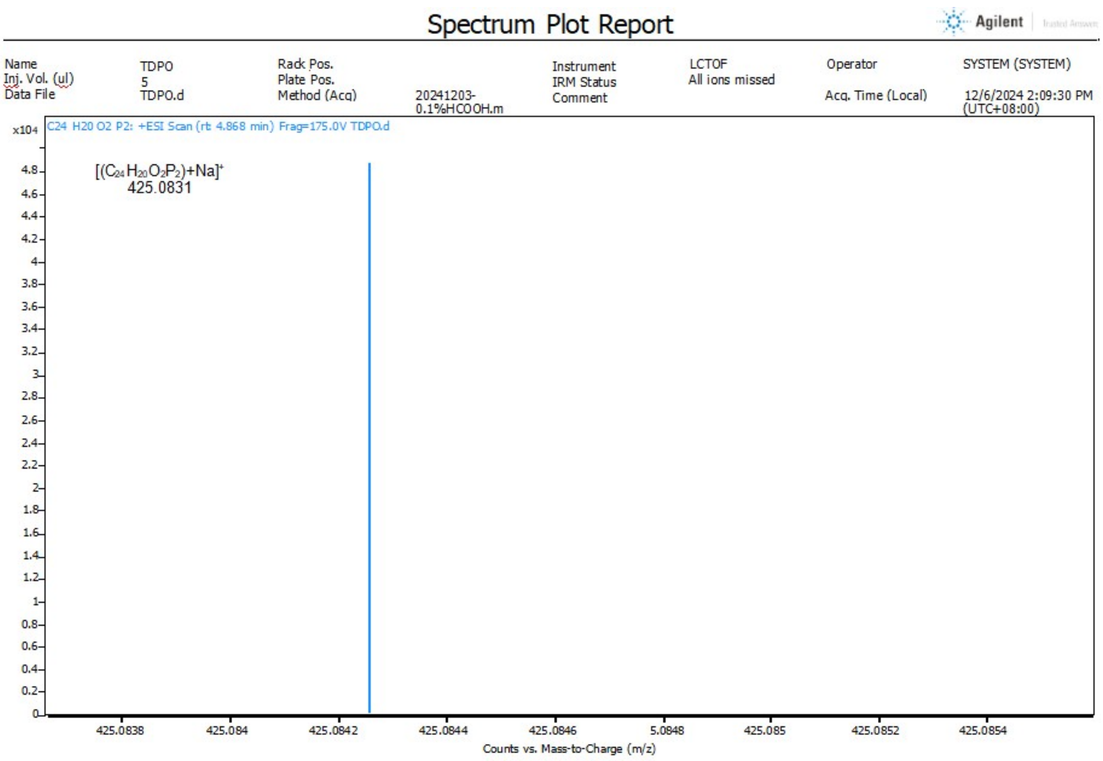
^{31}P NMR (162 MHz) Spectrum of 2a in DMSO-d^{6}



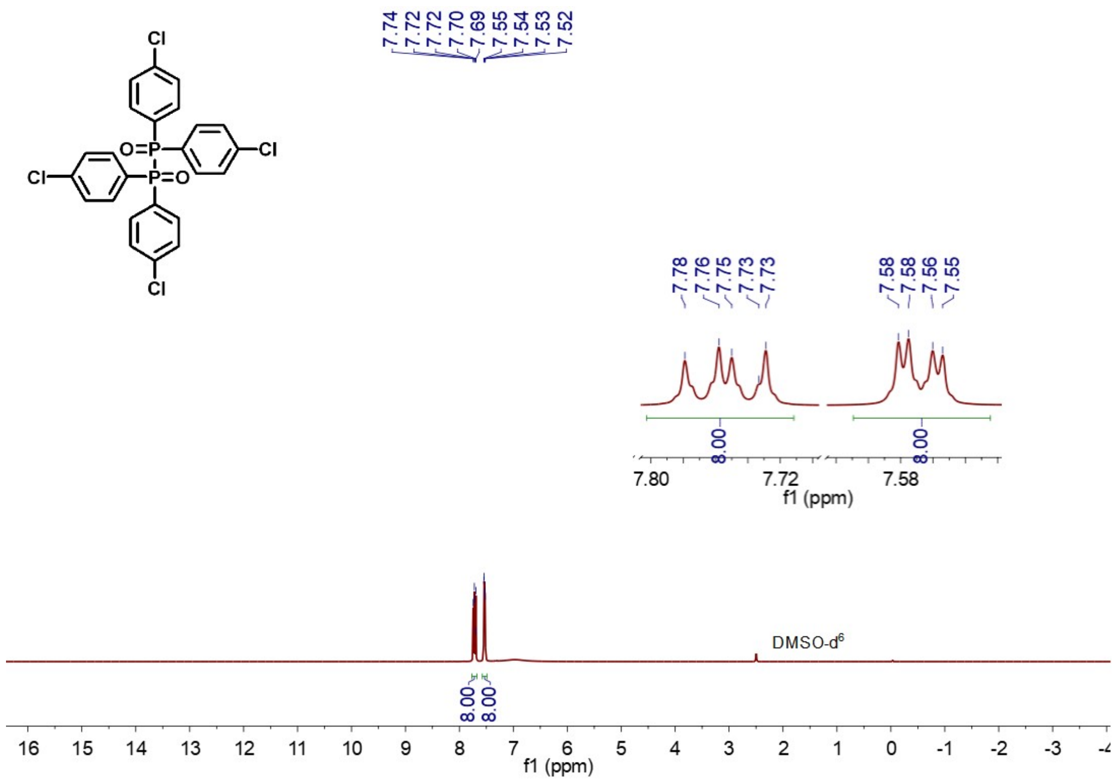
^{13}C NMR (101 MHz) Spectrum of 2a in DMSO-d^{6}



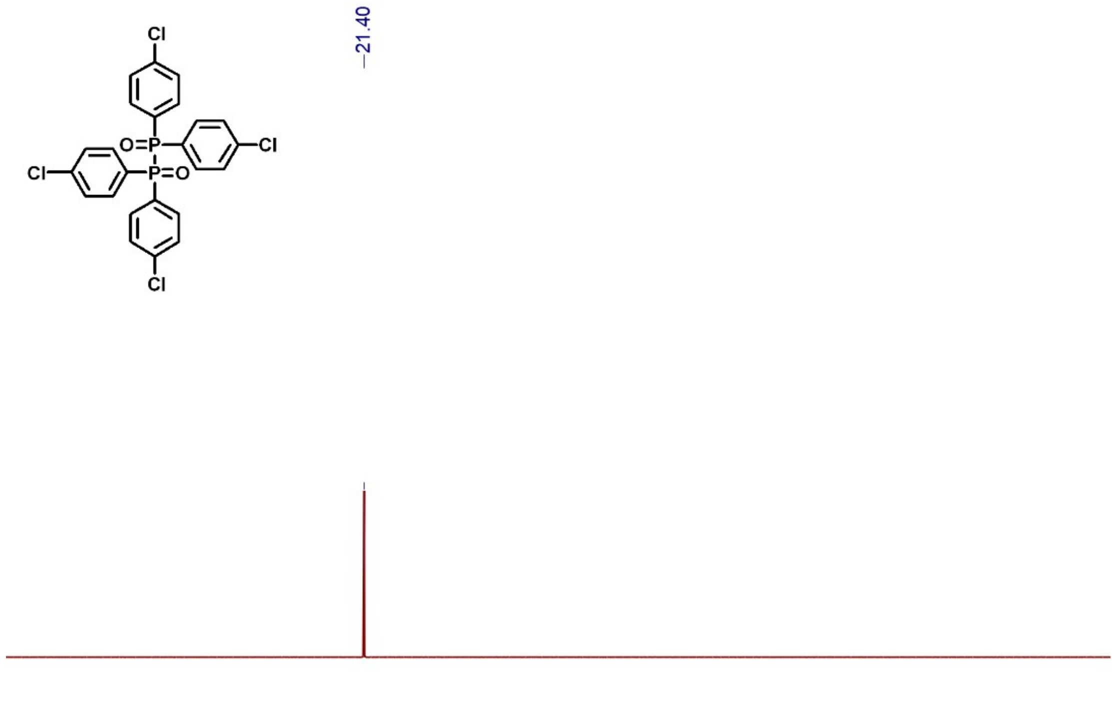
HRMS Spectrum of 2a



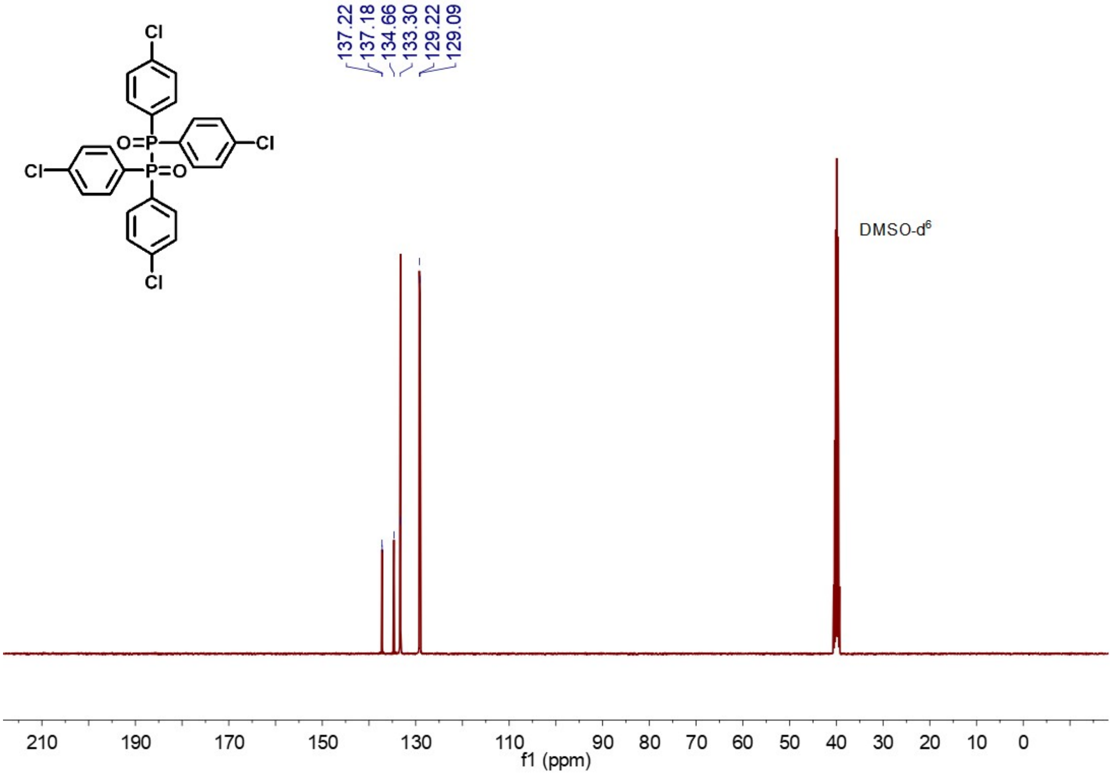
[1]HNMR (400 MHz) Spectrum of 2b in DMSO-d[6]



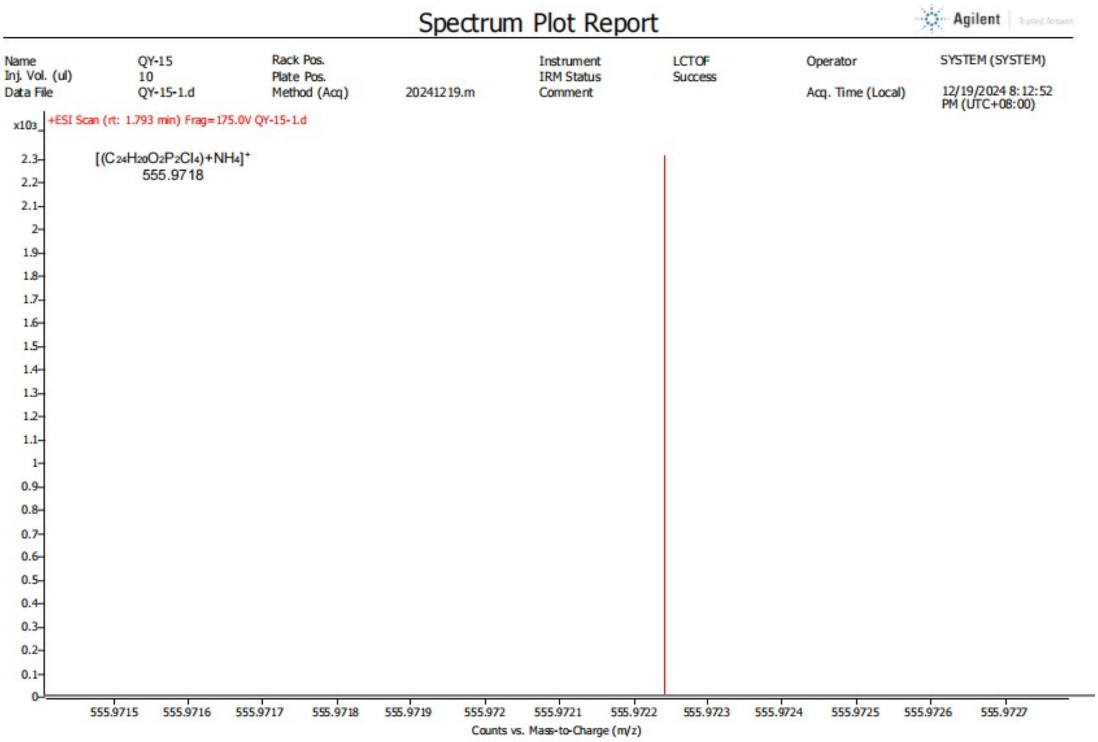
^{31}P NMR (162 MHz) Spectrum of 2b in DMSO-d^6



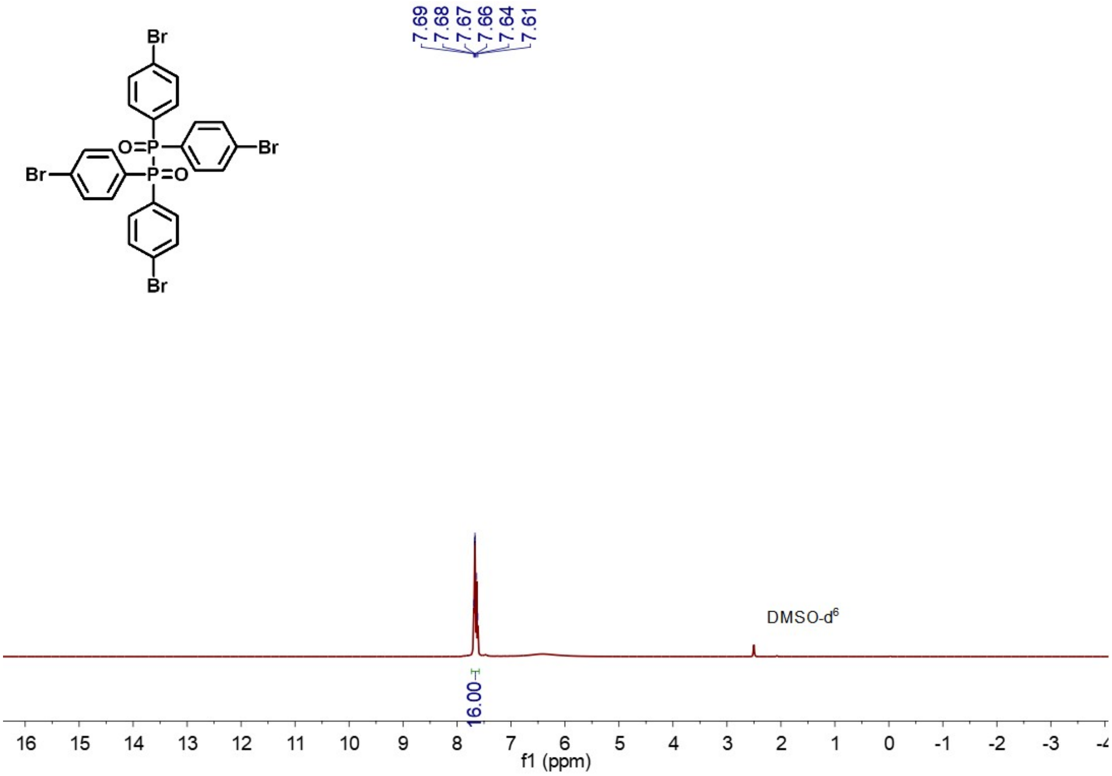
^{13}C NMR (101 MHz) Spectrum of 2b in DMSO-d6



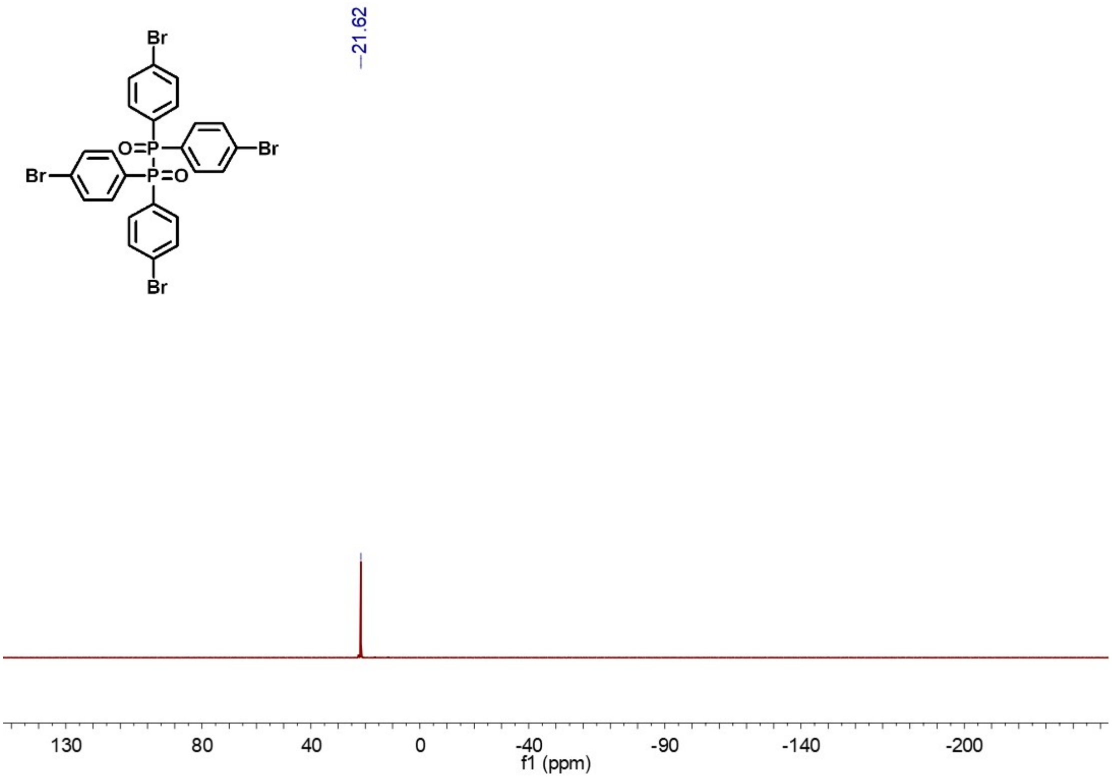
HRMS Spectrum of 2b



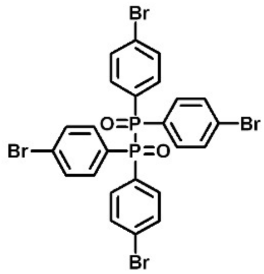
^{1}HNMR (400 MHz) Spectrum of 2c in DMSO-d^6

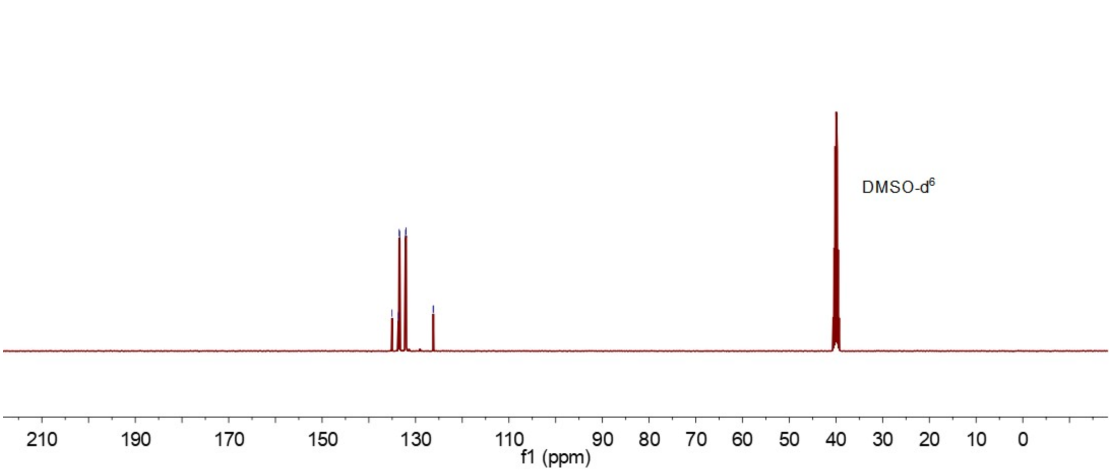


^{31}P NMR (162 MHz) Spectrum of 2c in DMSO-d^6

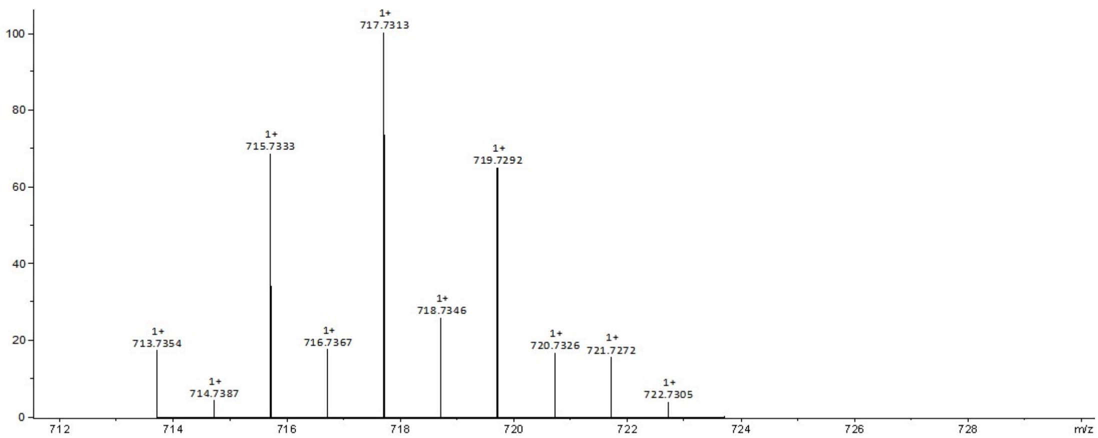


^{13}C NMR (101 MHz) Spectrum of 2c in DMSO-d[6]

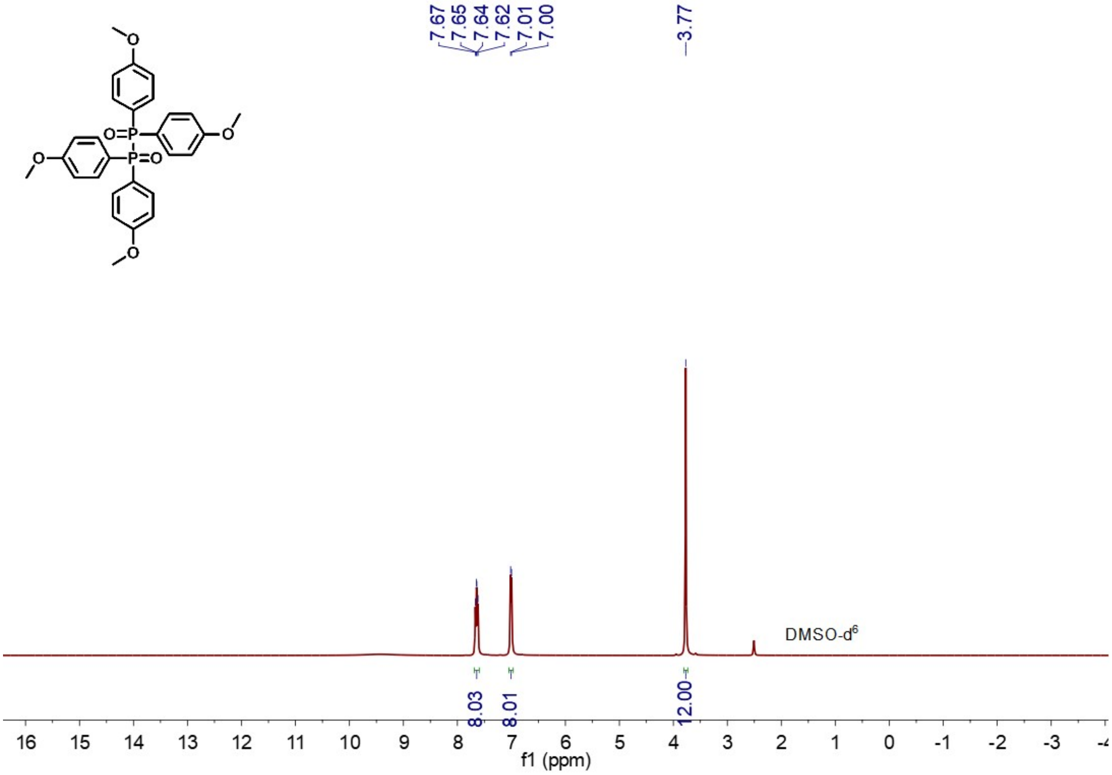




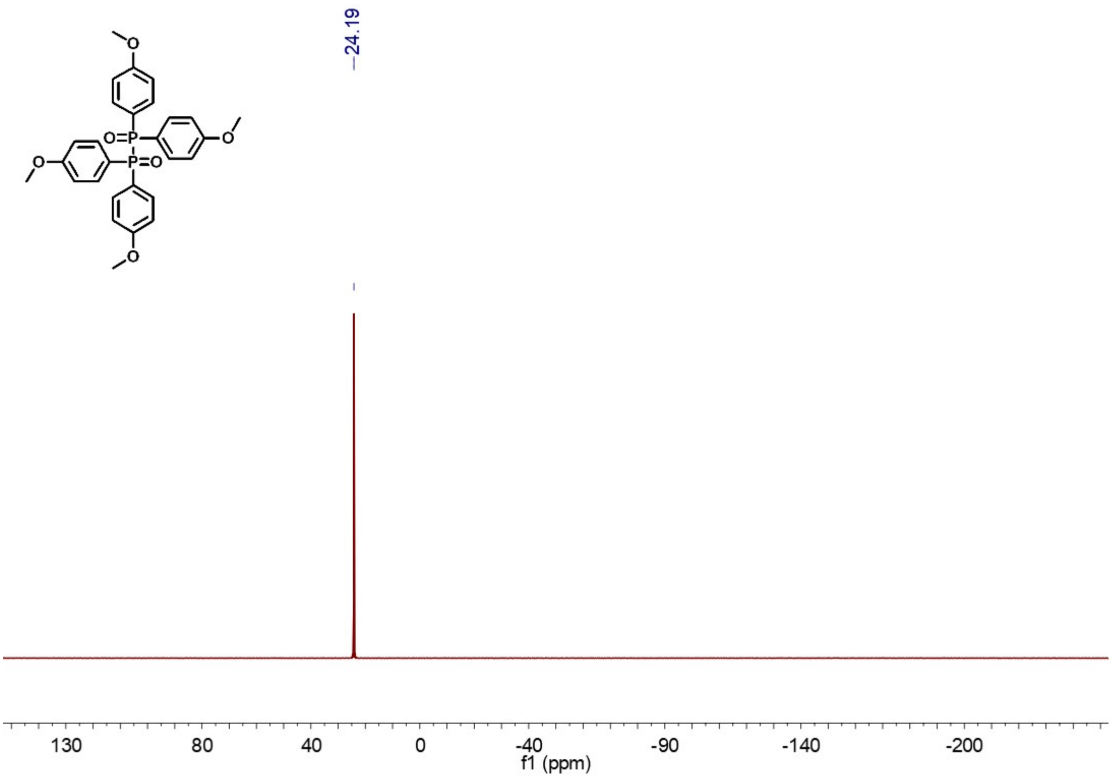
HRMS Spectrum of 2c



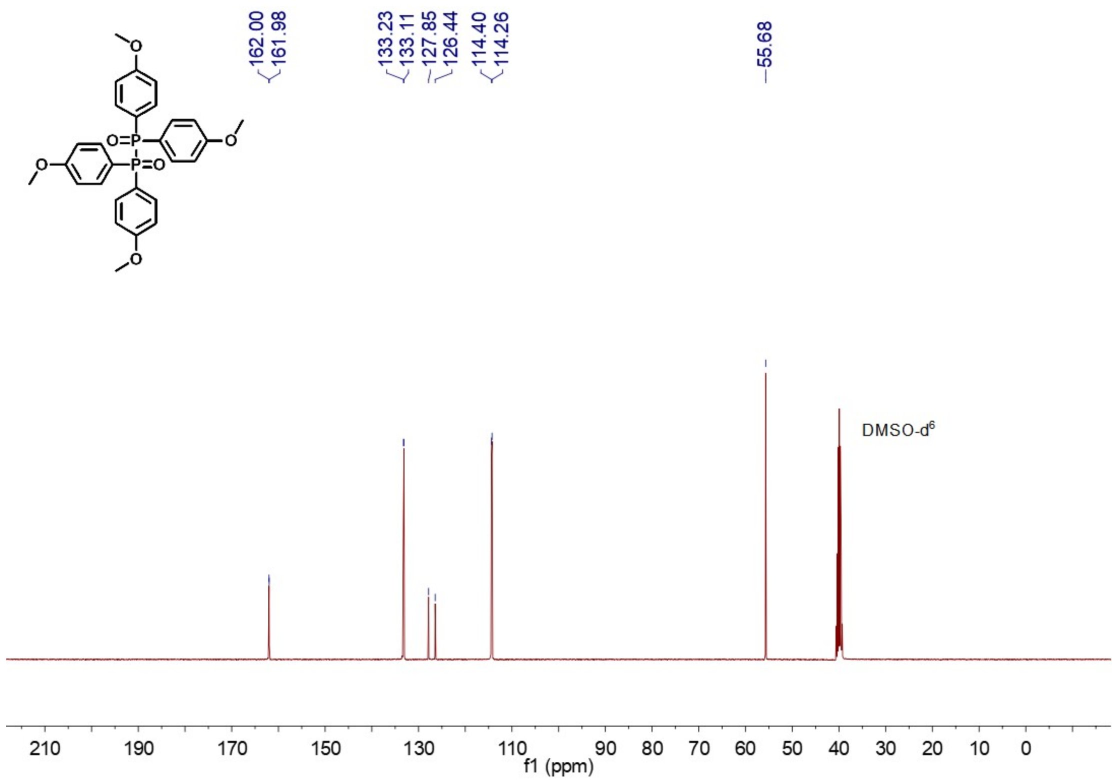
[1]HNMR (400 MHz) Spectrum of 2d in DMSO-d[6]



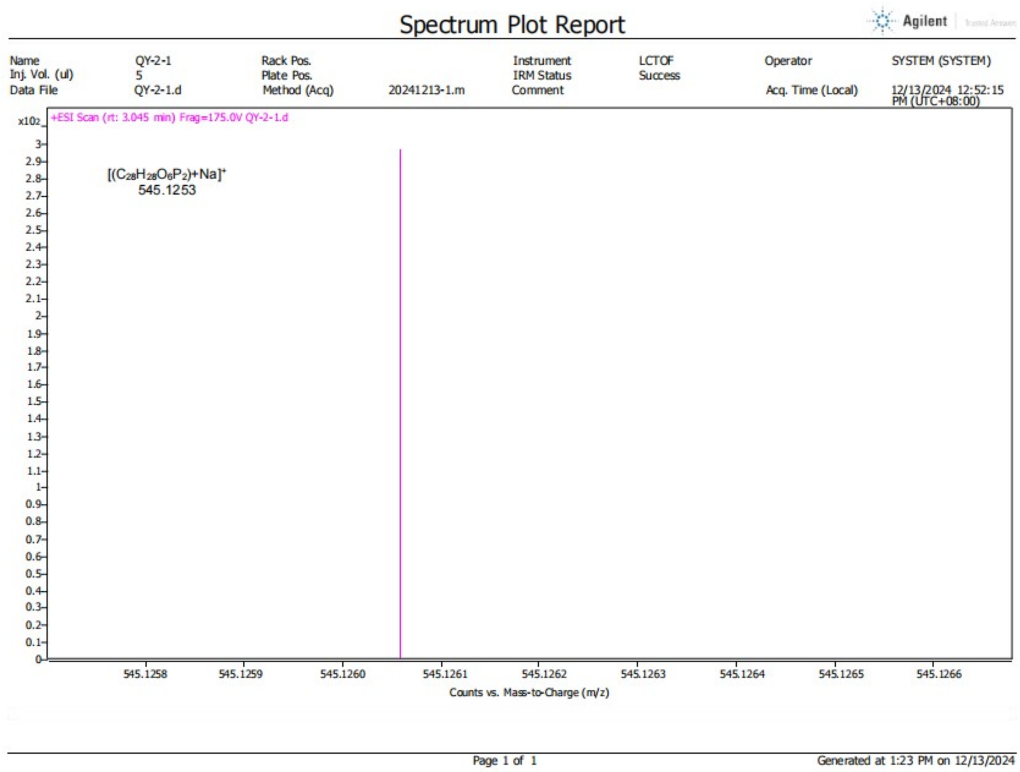
[31]P NMR (162 MHz) Spectrum of 2d in DMSO-d[6]



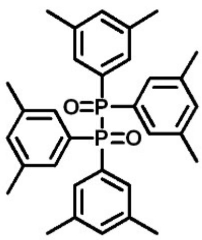
[13]C NMR (101 MHz) Spectrum of 2d in DMSO-d[6]

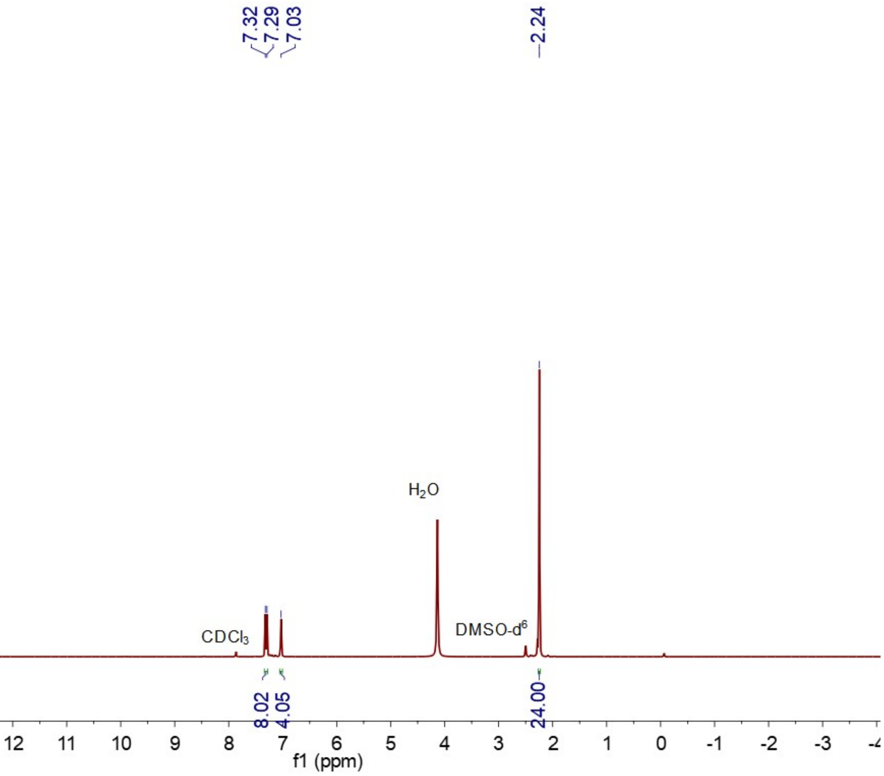


HRMS Spectrum of 2d

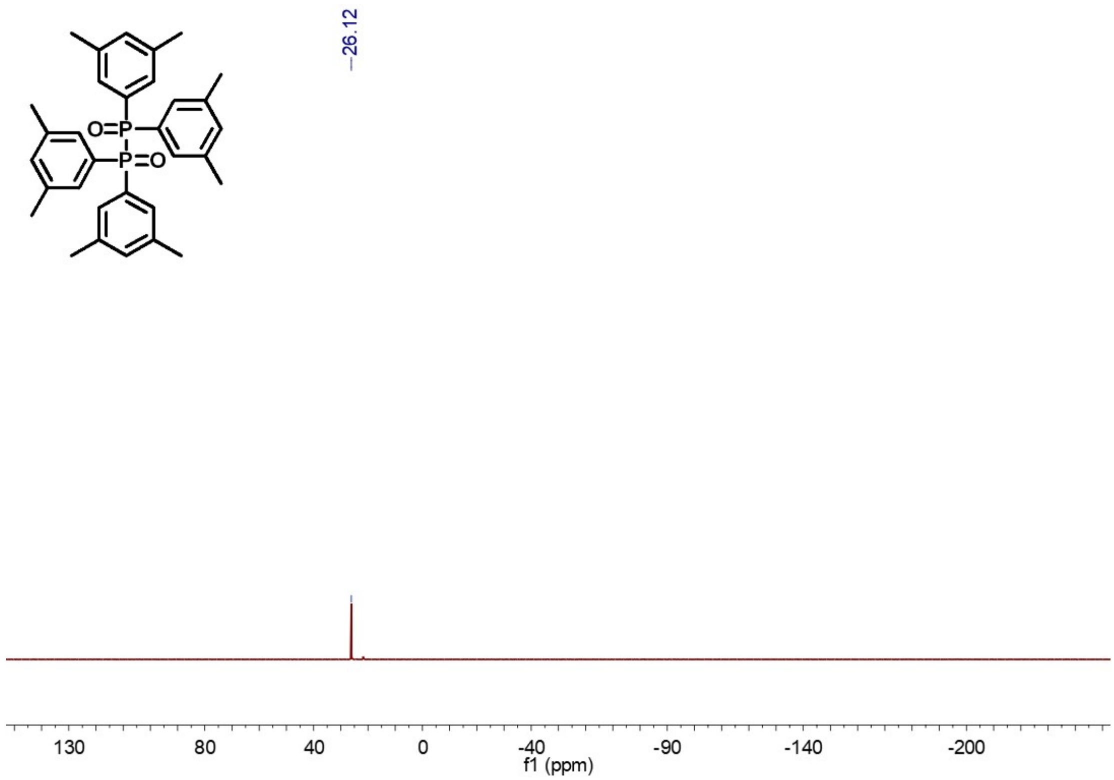


^{1}HNMR (400 MHz) Spectrum of 2e in DMSO-d^6 and $CDCl_3$

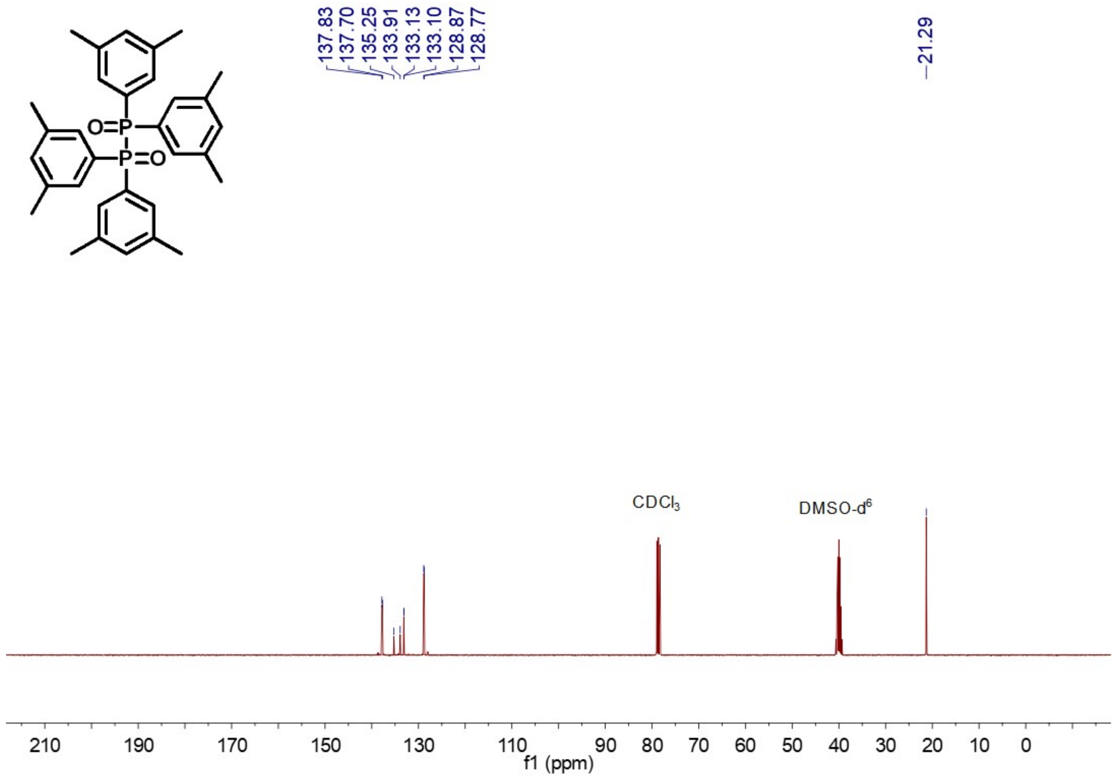



7.32
7.29
7.03
2.24
H_2O
$CDCl_3$
DMSO-d6
8.02
4.05
24.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

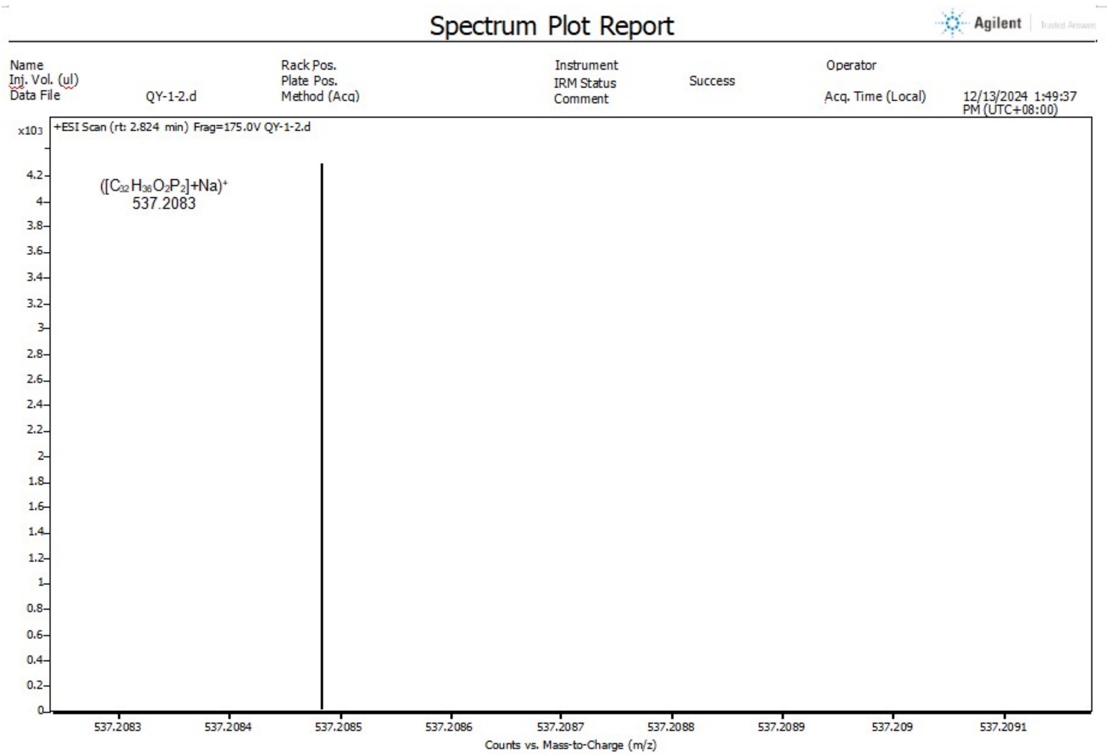
^{31}P NMR (162 MHz) Spectrum of 2e in DMSO-d^6 and $CDCl_3$



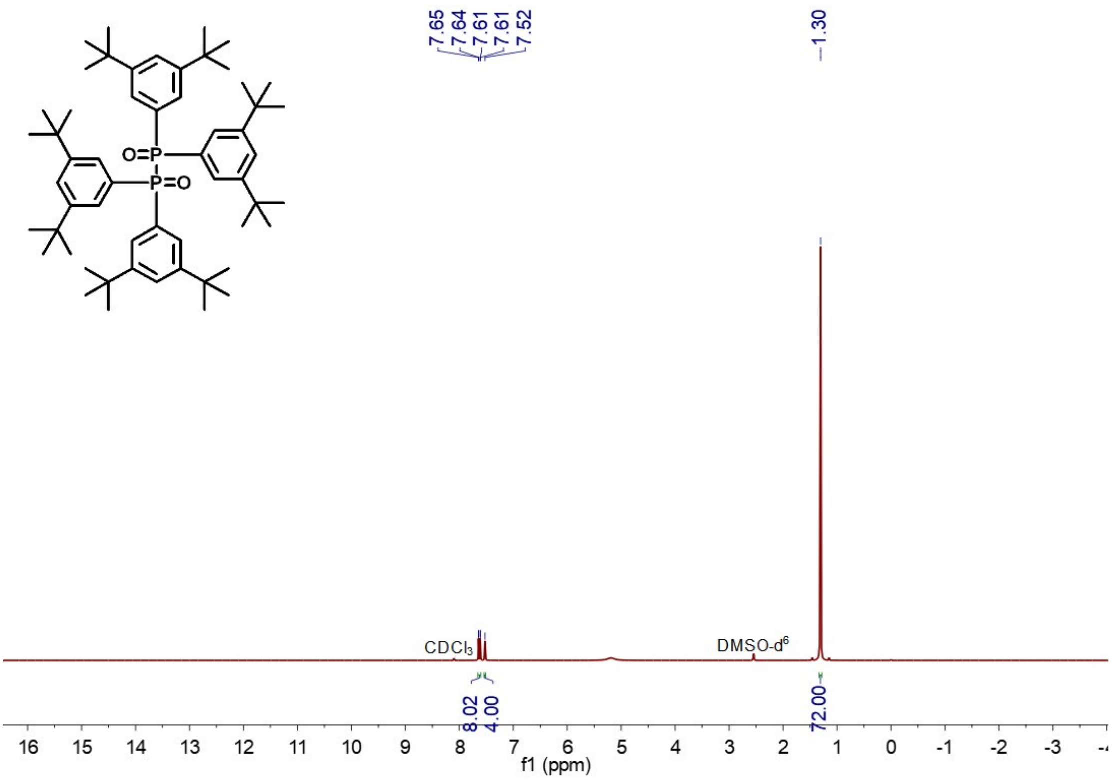
^{13}C NMR (101 MHz) Spectrum of 2e in DMSO-d^6 and $CDCl_3$



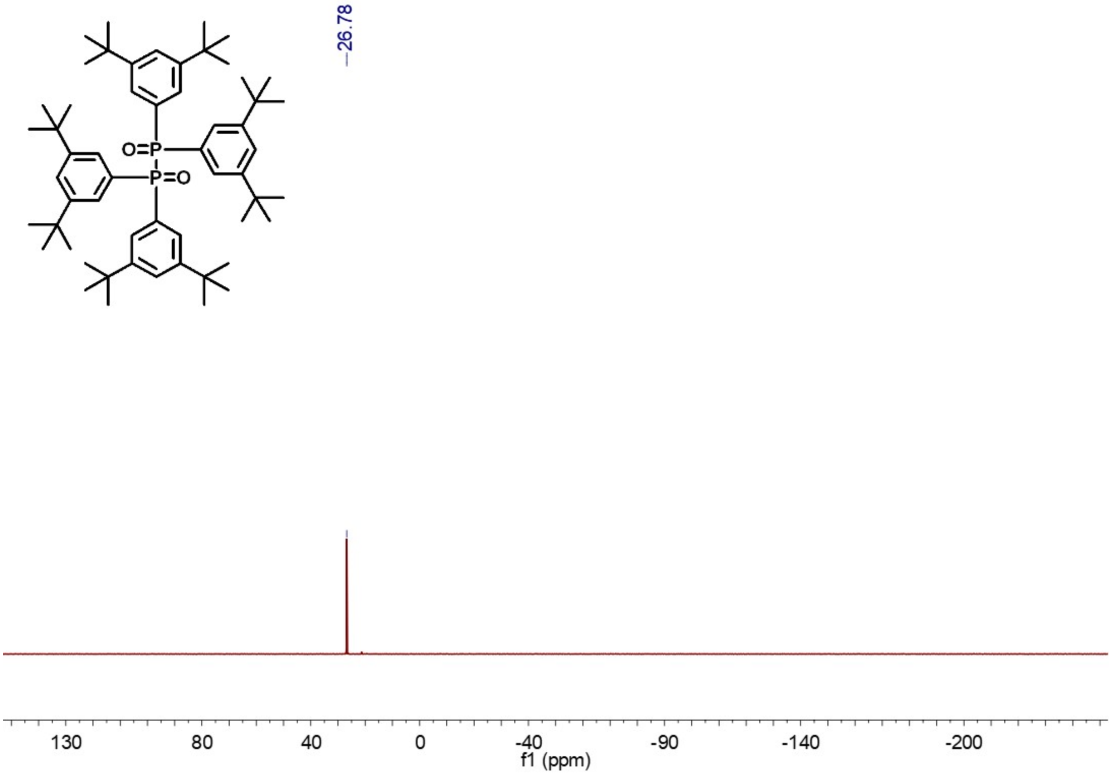
HRMS Spectrum of 2e



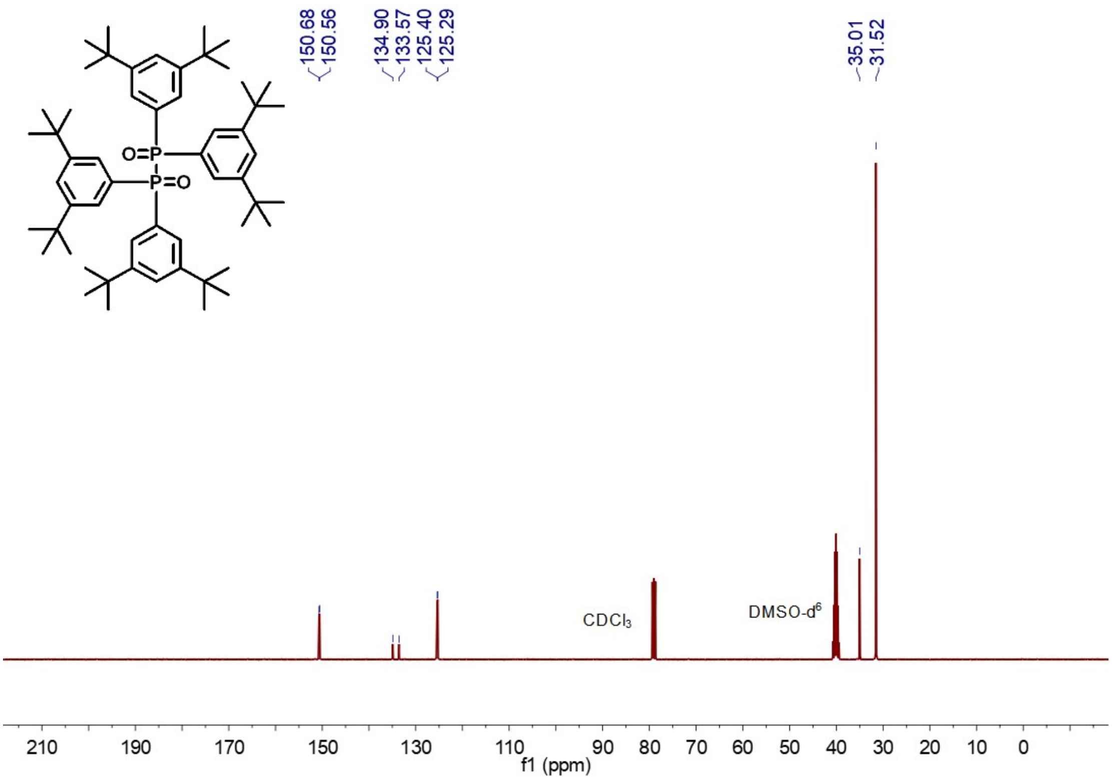
[1]HNMR (400 MHz) Spectrum of 2f in DMSO-d^6 and $CDCl_3$



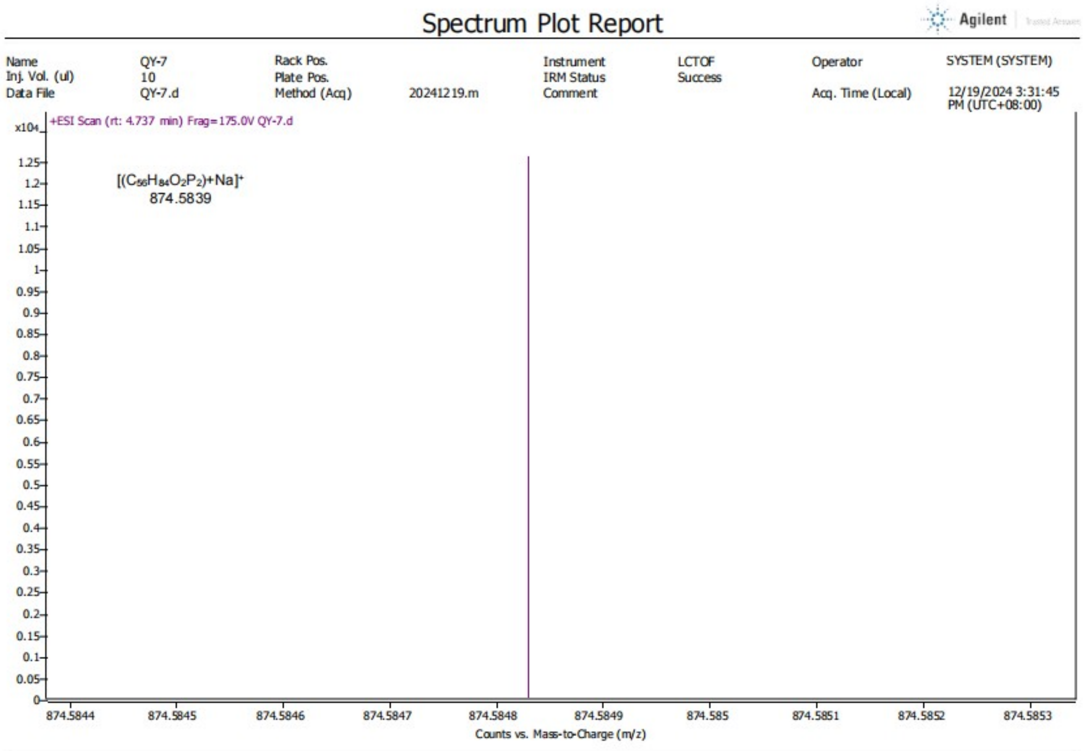
^{31}P NMR (162 MHz) Spectrum of 2f in DMSO-d^6 and CDCl$_3$



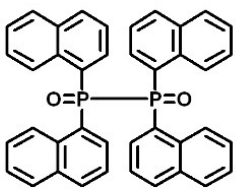
^{13}C NMR (101 MHz) Spectrum of 2f in DMSO-d^6 and CDCl$_3$

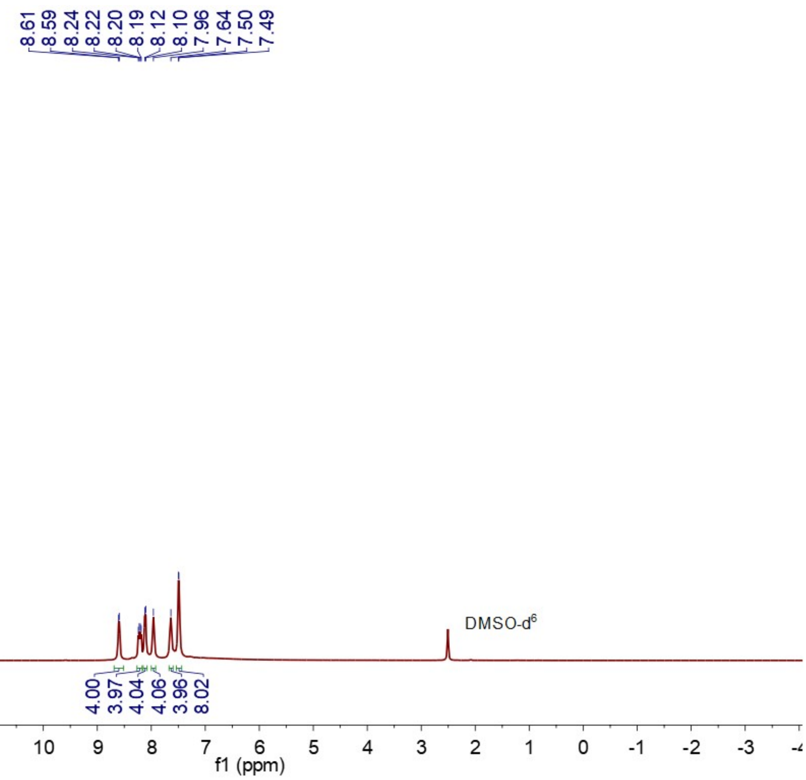


HRMS Spectrum of 2f

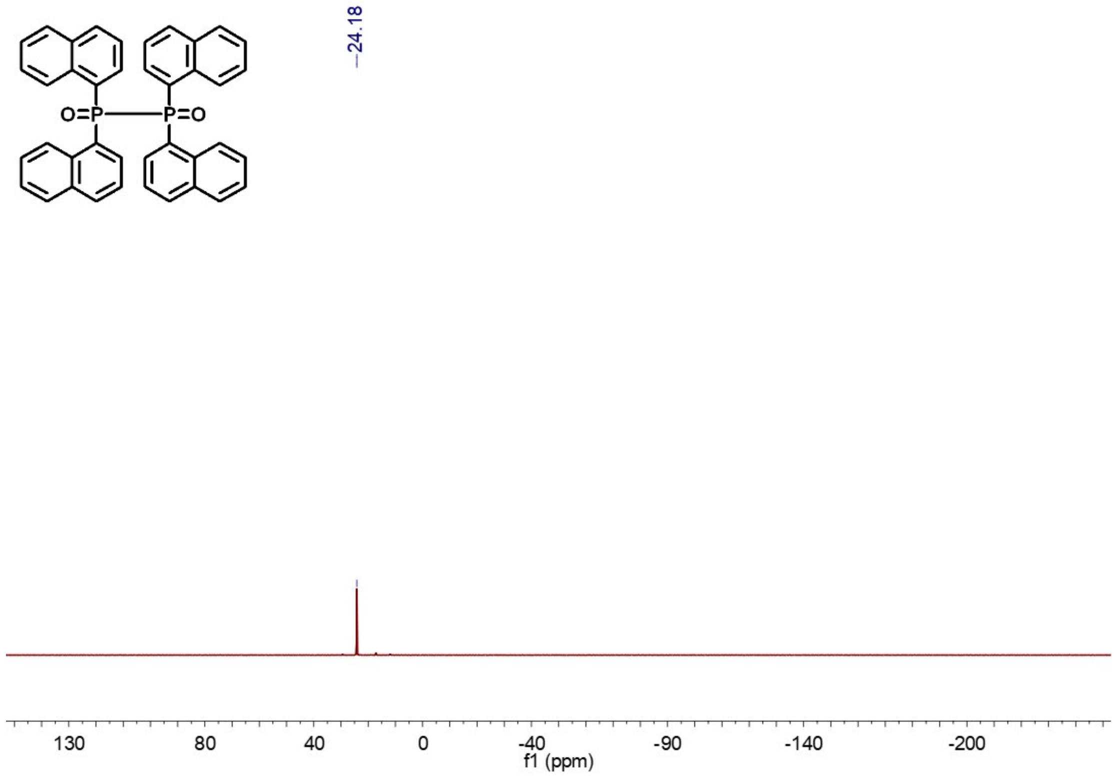


[1]HNMR (400 MHz) Spectrum of 2g in DMSO-d[6]

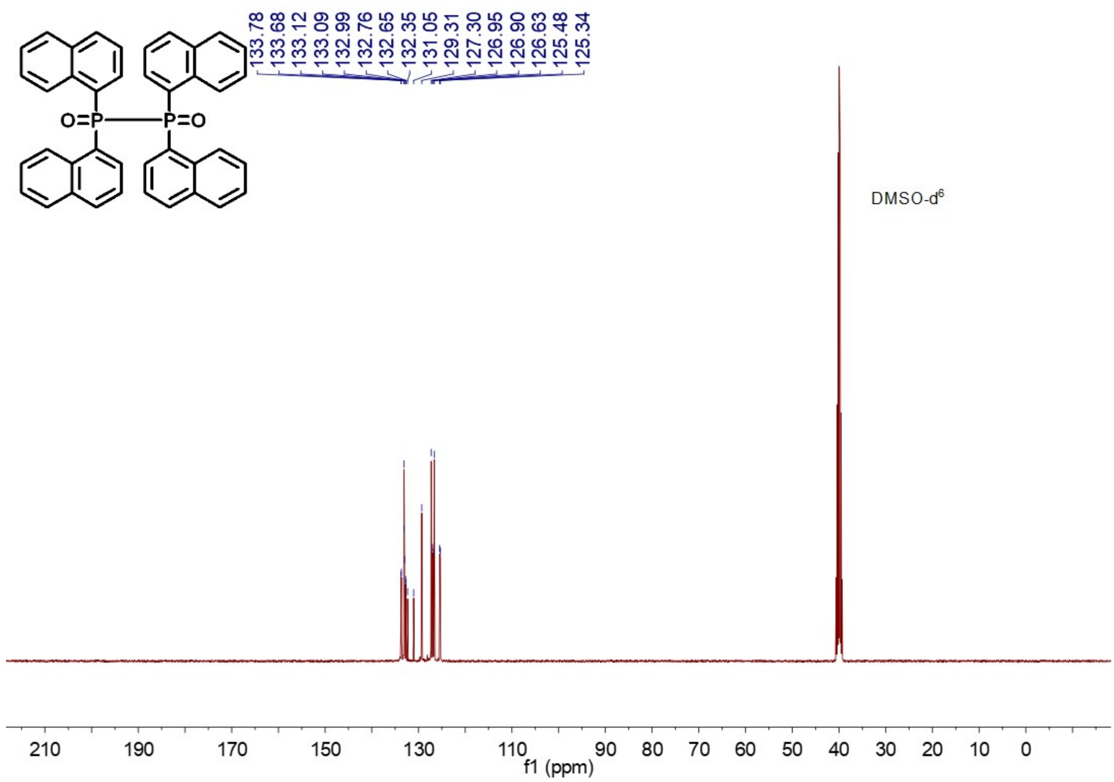




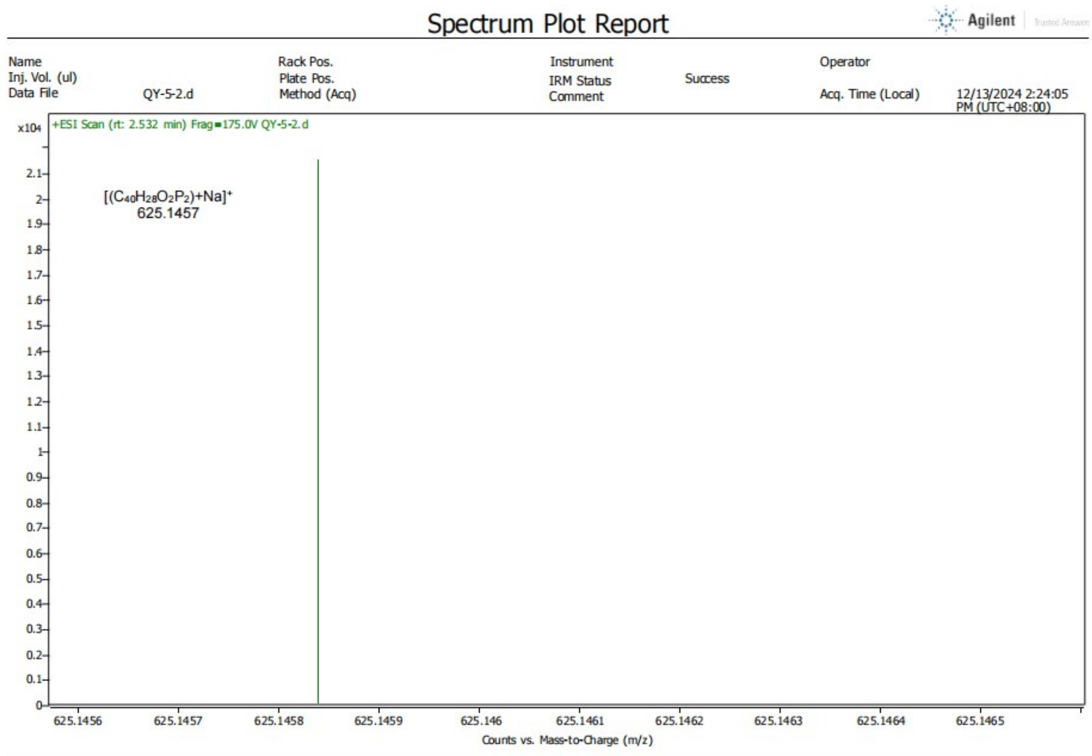
^{31}P NMR (162 MHz) Spectrum of 2g in DMSO-d6



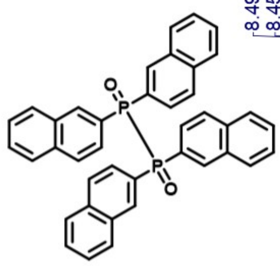
^{13}C NMR (101 MHz) Spectrum of 2g in DMSO-d6

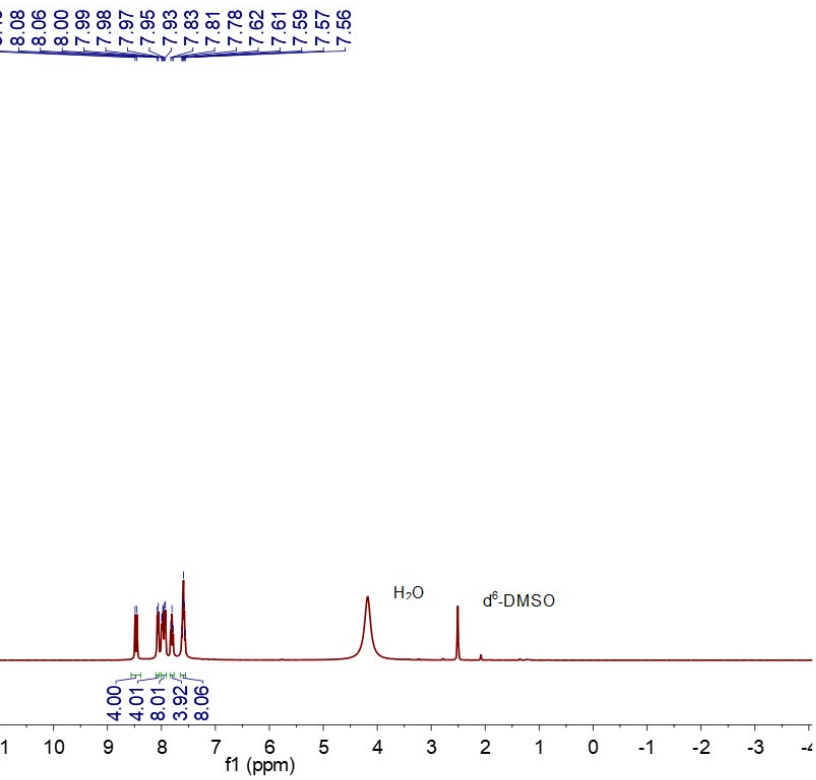


HRMS Spectrum of 2g

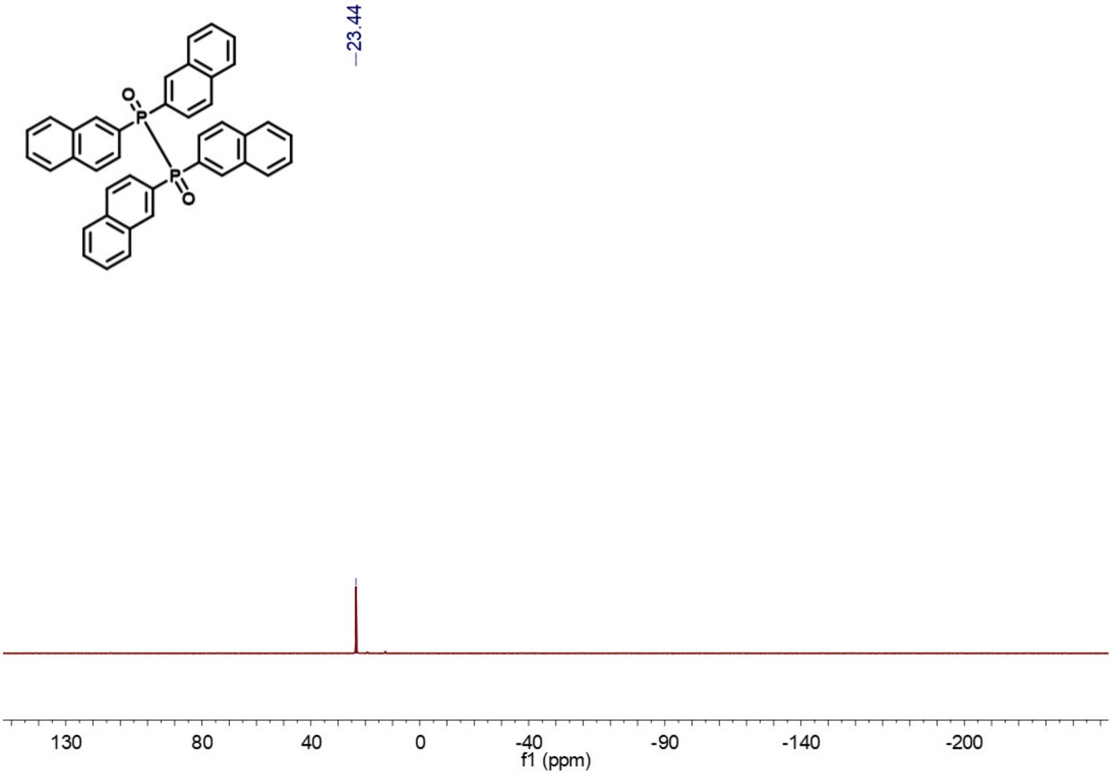


[1]HNMR (400 MHz) Spectrum of 2h in DMSO-d[6]

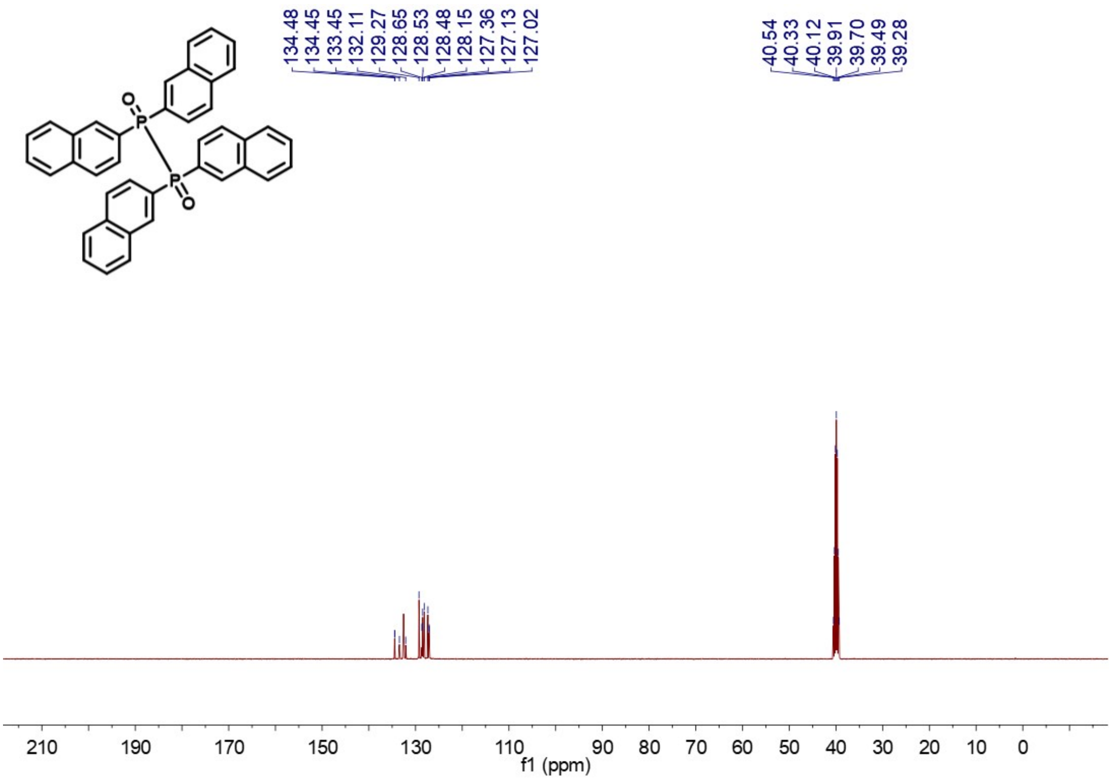




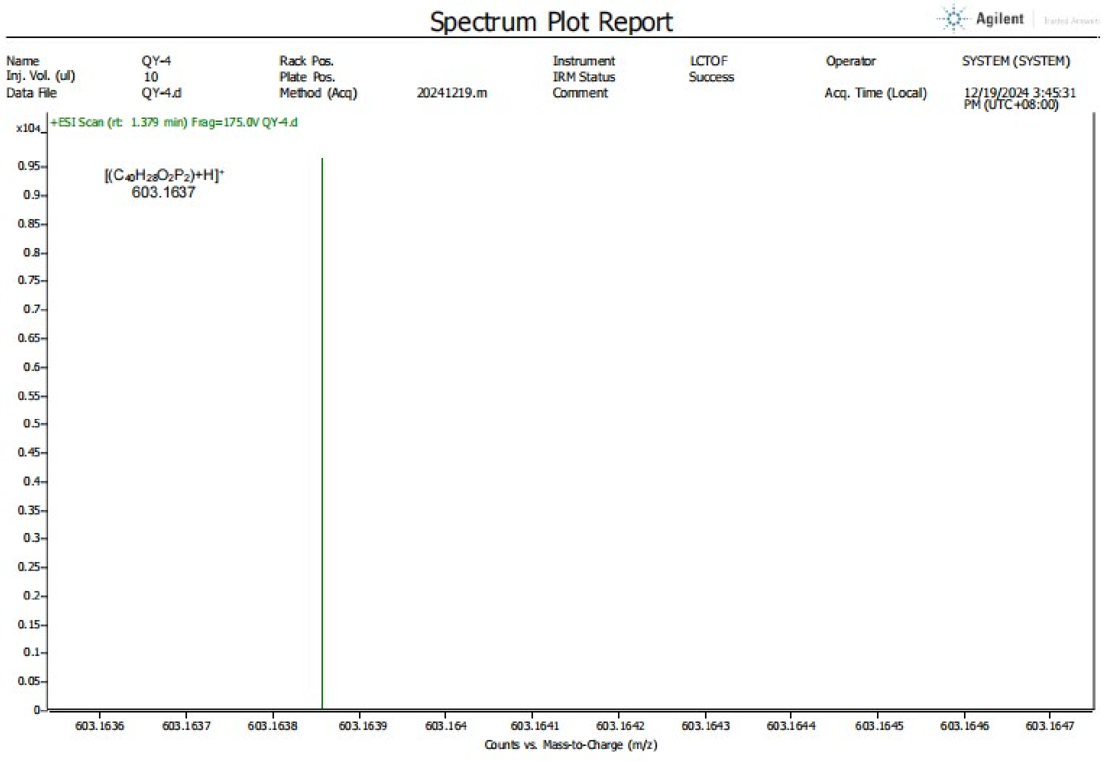
^{31}P NMR (162 MHz) Spectrum of 2h in DMSO-d^{6}



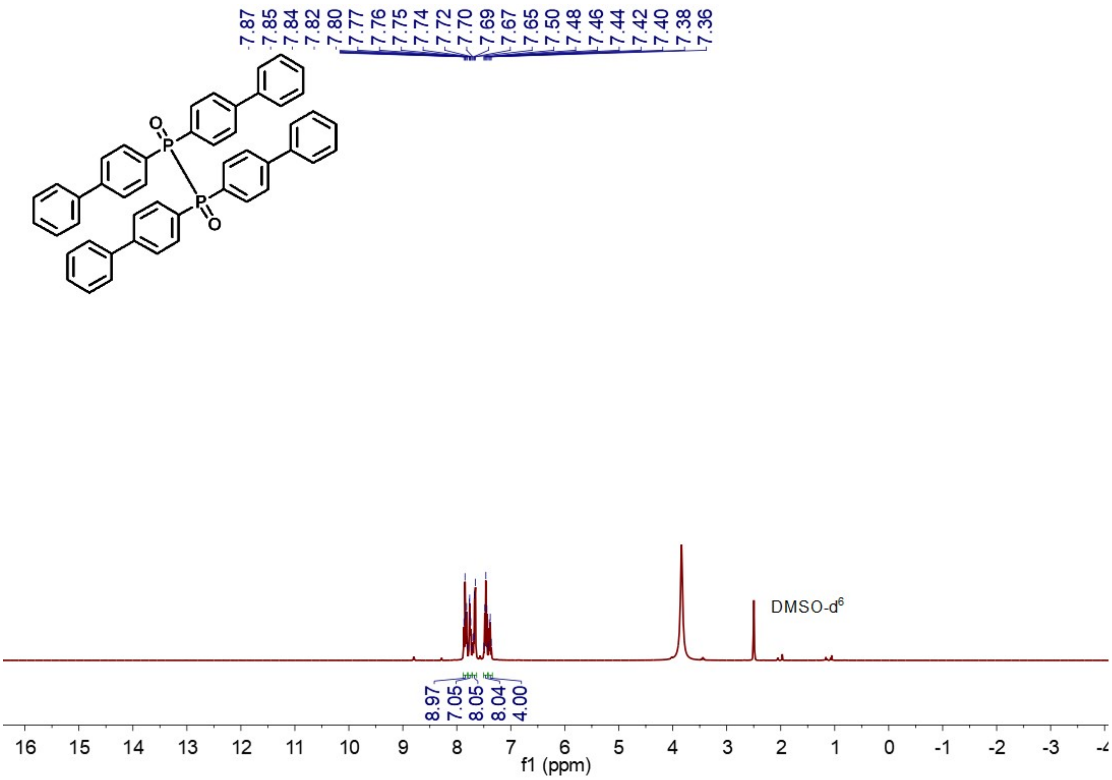
^{13}C NMR (101 MHz) Spectrum of 2h in DMSO-d^{6}



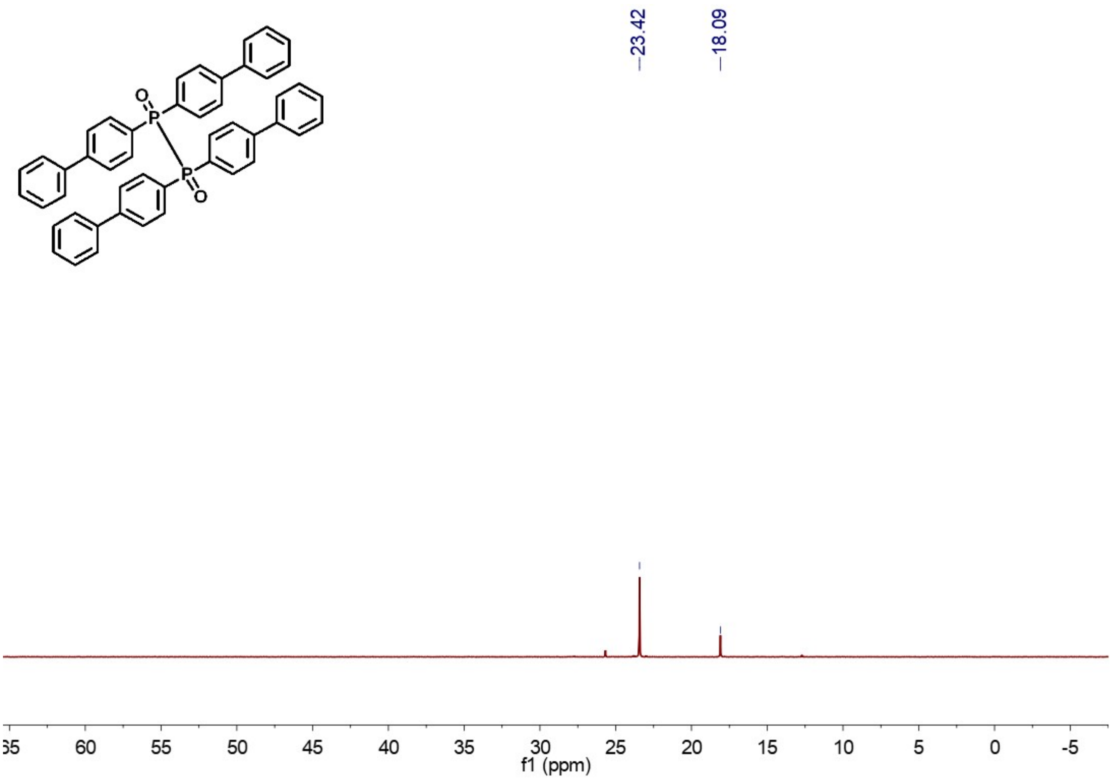
HRMS Spectrum of 2h



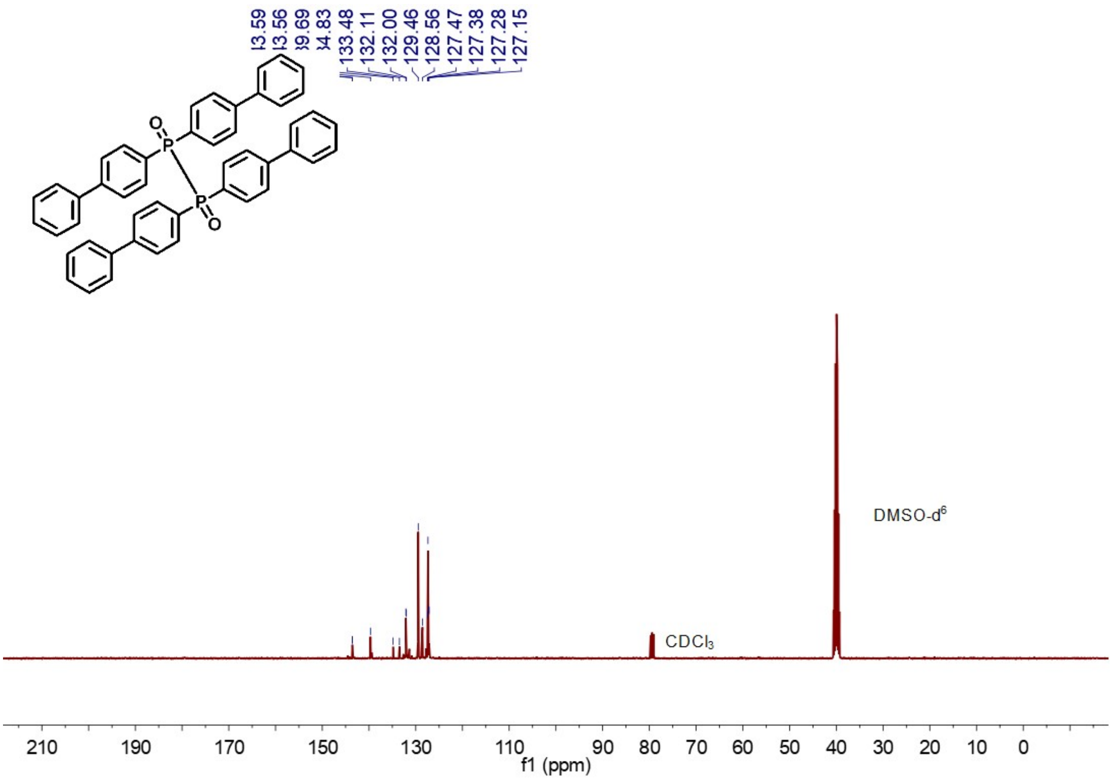
^{1}HNMR (400 MHz) Spectrum of 2i in DMSO-d^6 and CDCl$_3$



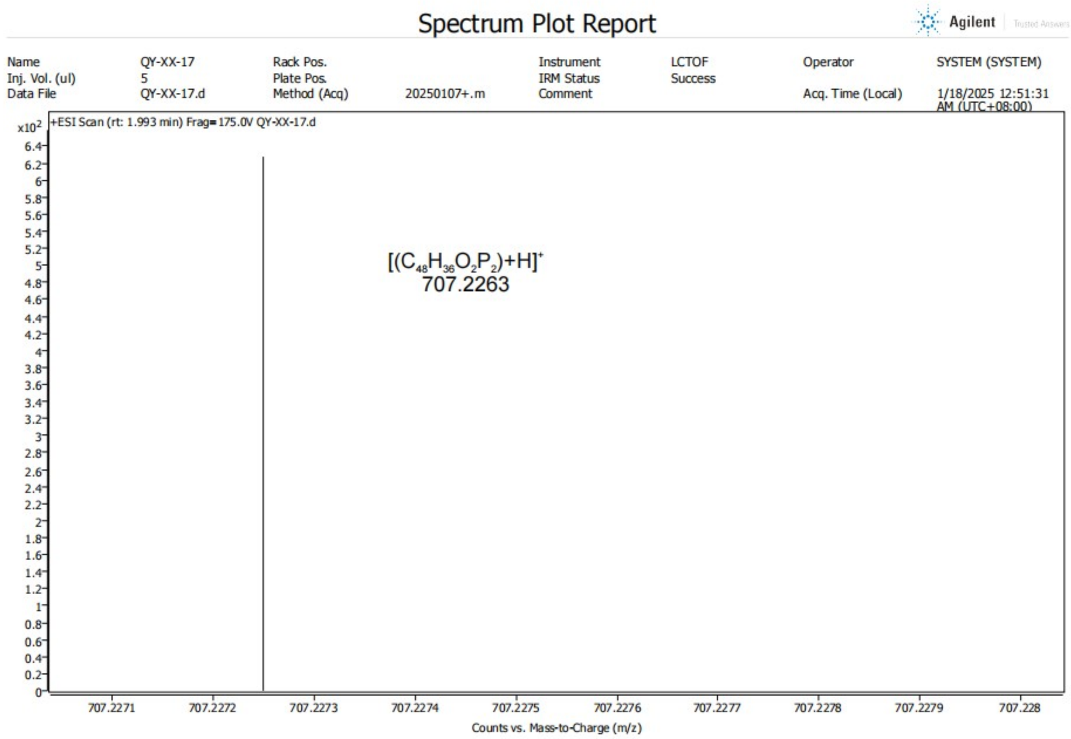
^{31}P NMR (162 MHz) Spectrum of 2i in DMSO-d^6 and $CDCl_3$



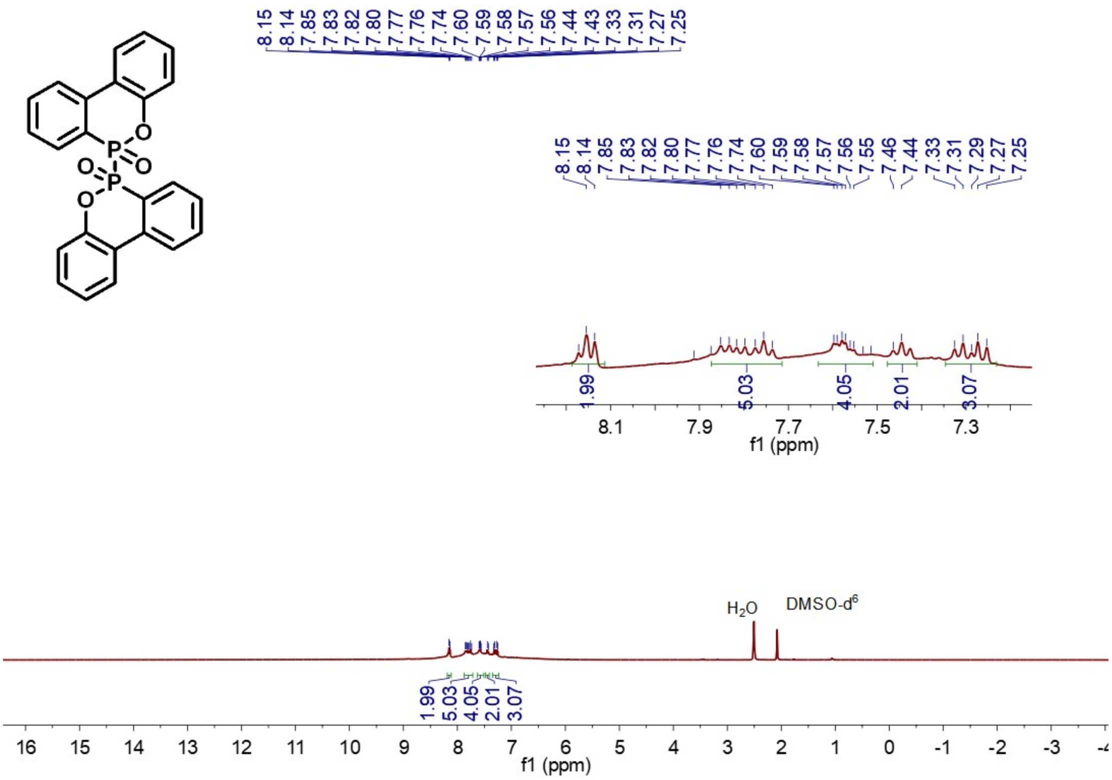
^{13}C NMR (101 MHz) Spectrum of 2i in DMSO-d^6 and $CDCl_3$



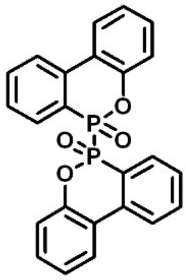
HRMS Spectrum of 2i

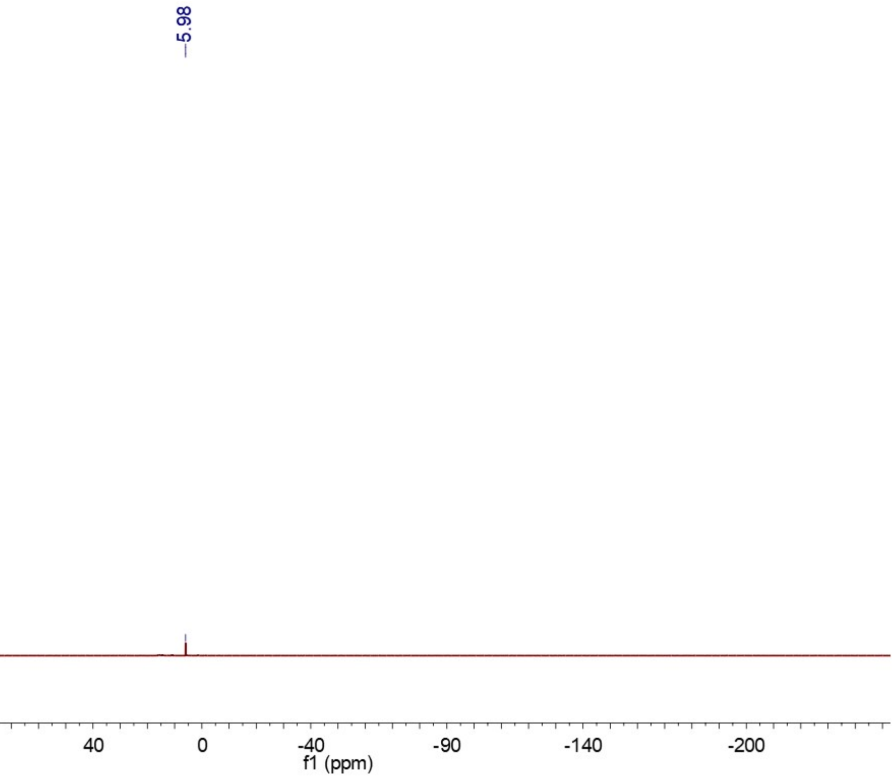


^{1}HNMR (400 MHz) Spectrum of 2j in DMSO-d^6

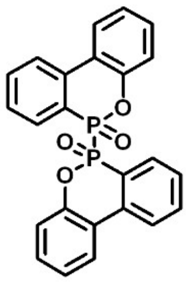


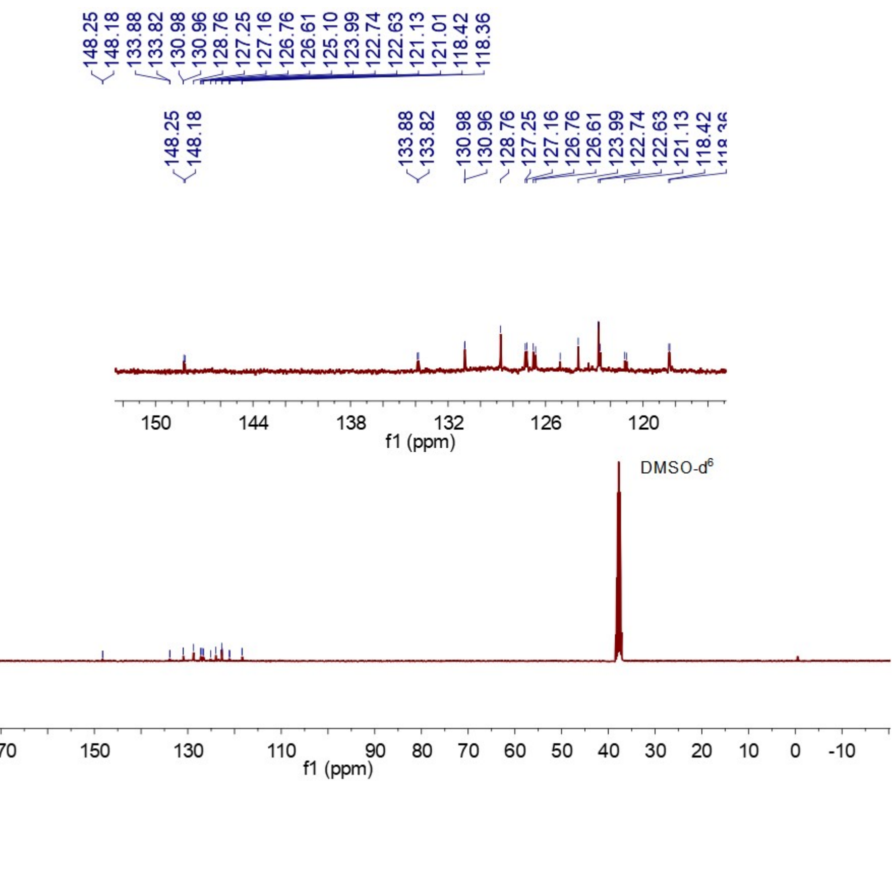
^{31}P NMR (162 MHz) Spectrum of 2j in DMSO-d[6]



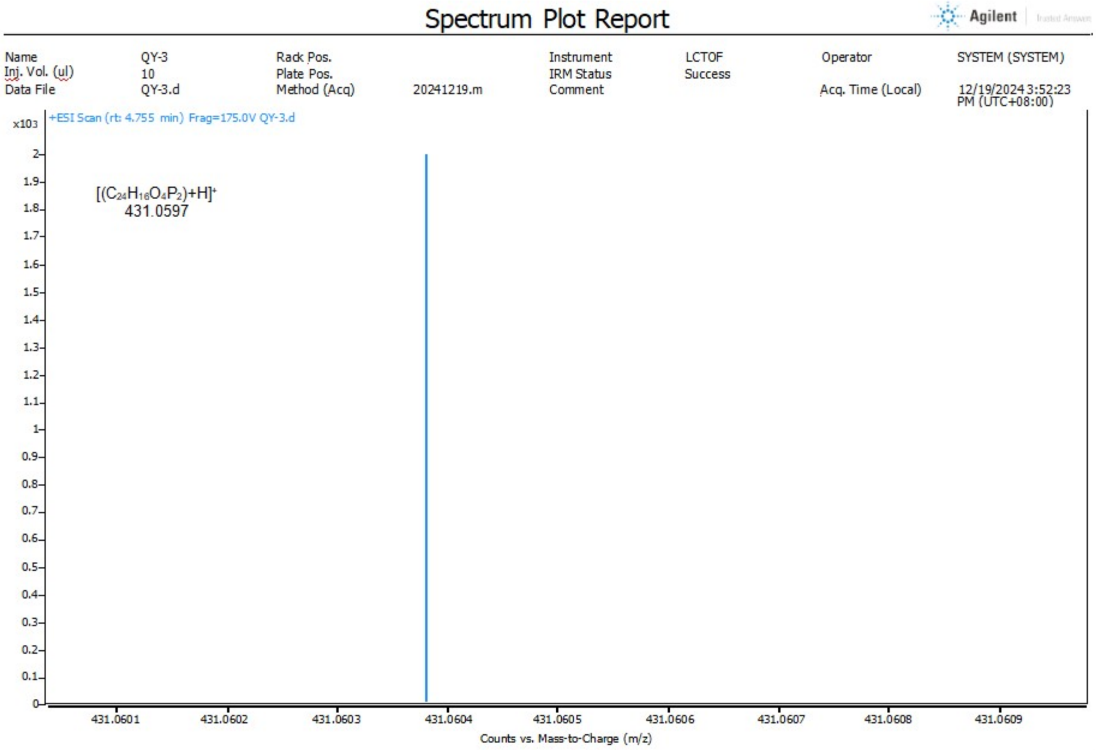


^{13}C NMR (101 MHz) Spectrum of 2j in DMSO-d[6]

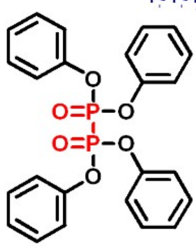


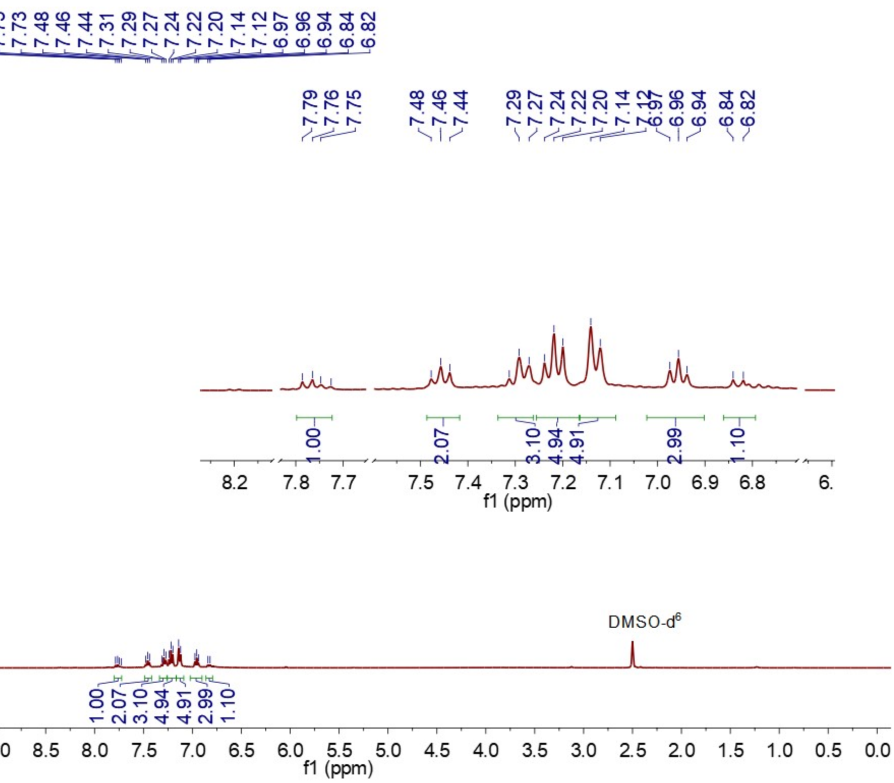


HRMS Spectrum of 2j

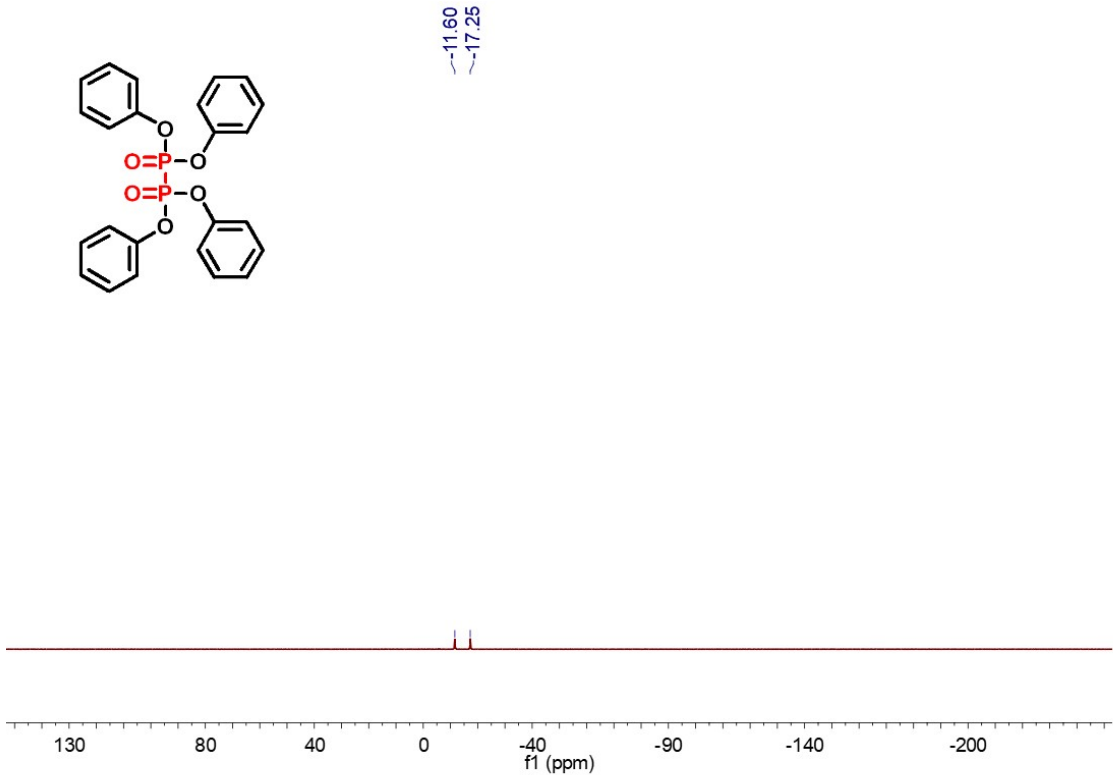


[1]HNMR (400 MHz) Spectrum of 2k in DMSO-d[6]

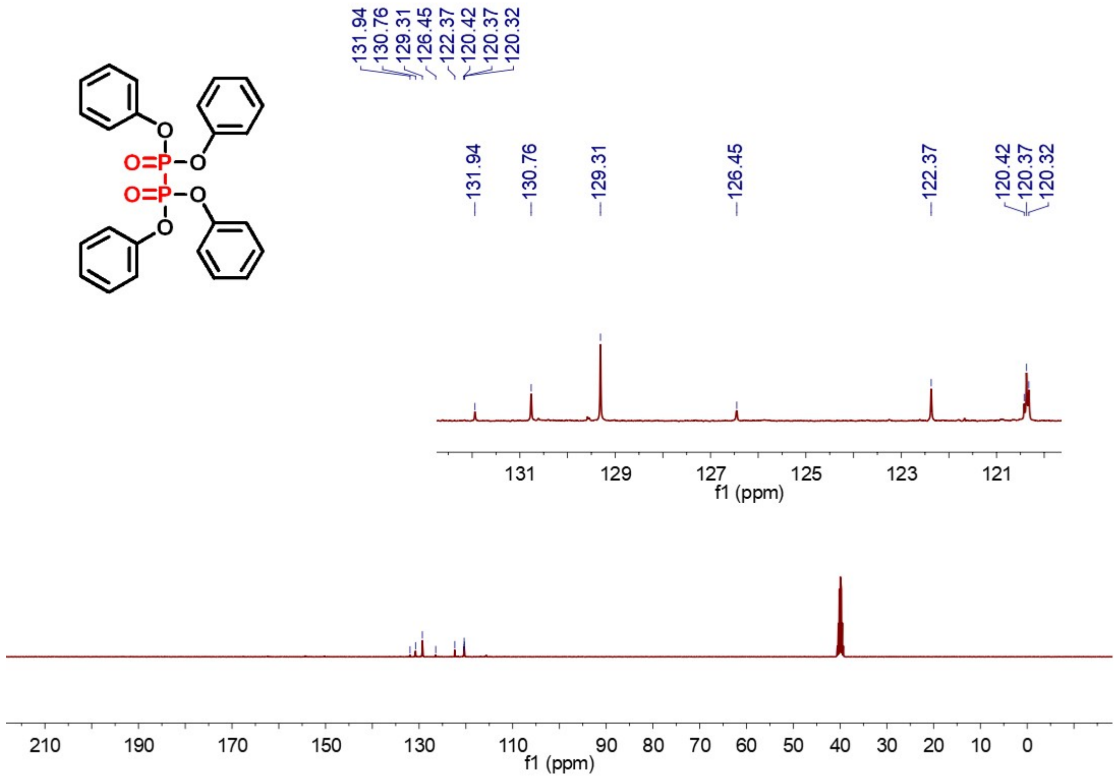




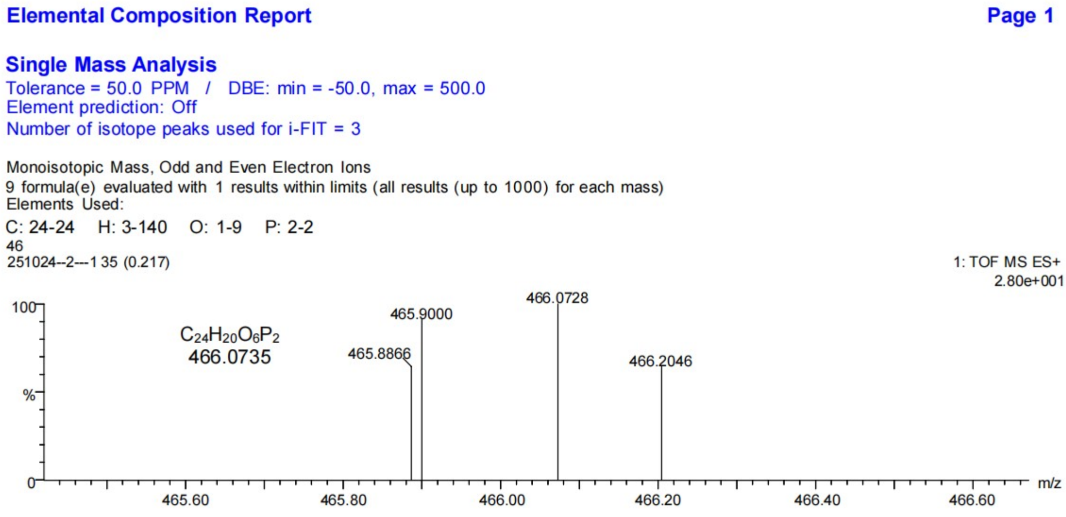
^{31}P NMR (162 MHz) Spectrum of 2k in DMSO-d^6



^{13}C NMR (101 MHz) Spectrum of 2k in DMSO-d^6



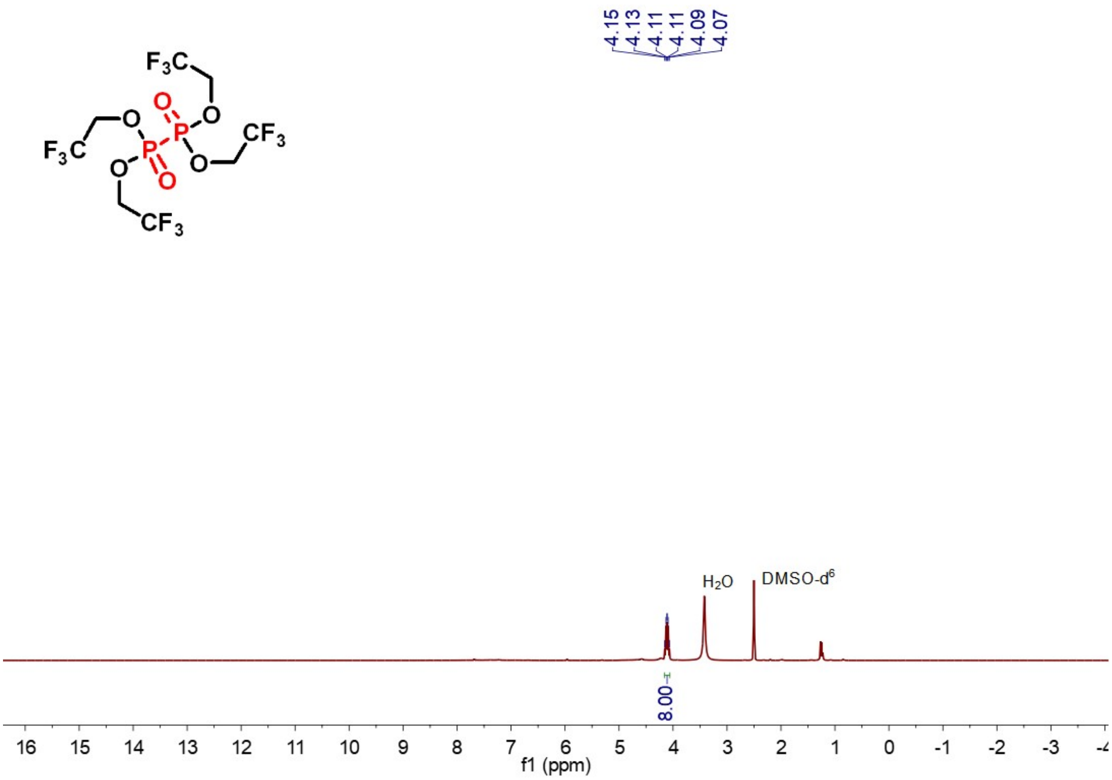
HRMS Spectrum of 2k



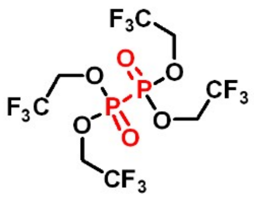
Minimum:				-50.0				
Maximum:		5.0	50.0	500.0				

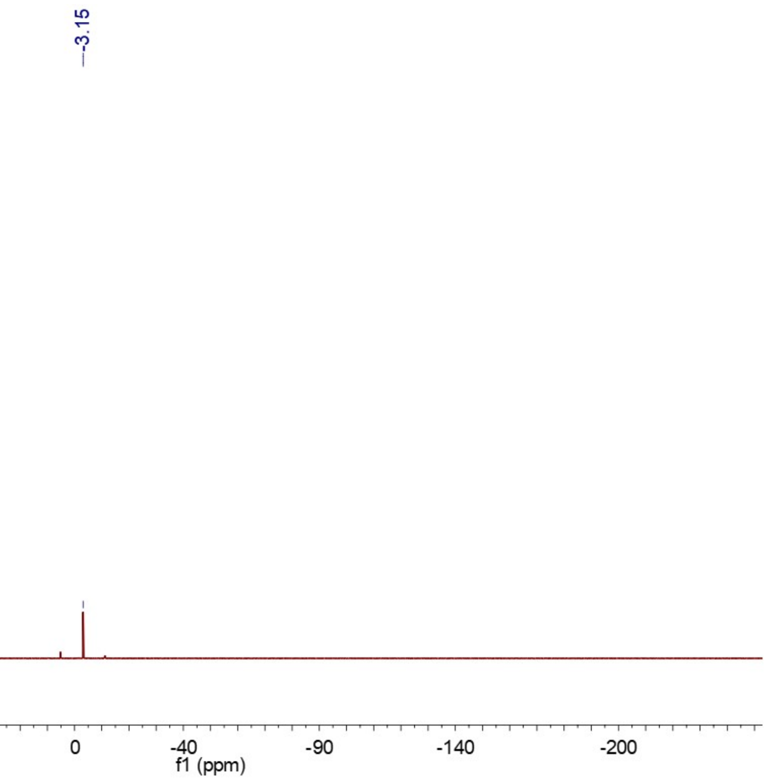
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
466.0728	466.0735	-0.7	-1.5	16.0	19.9	n/a	n/a	C24 H20 O6 P2

^{1}HNMR (400 MHz) Spectrum of 2l in DMSO-d^6

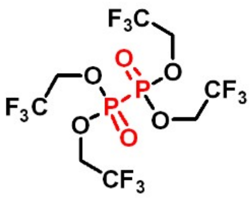


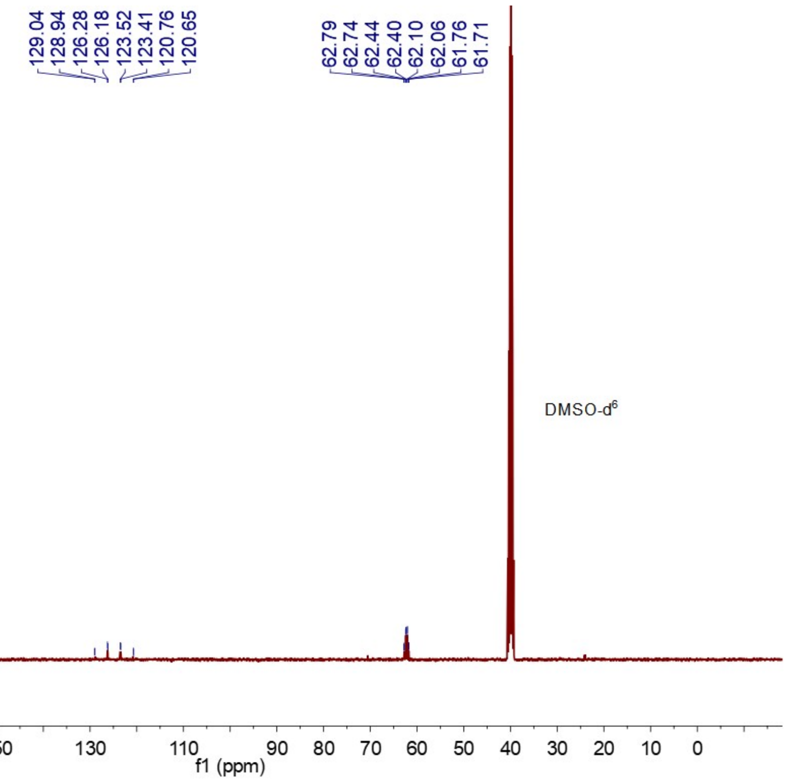
^{31}P NMR (162 MHz) Spectrum of 2l in DMSO-d⁶



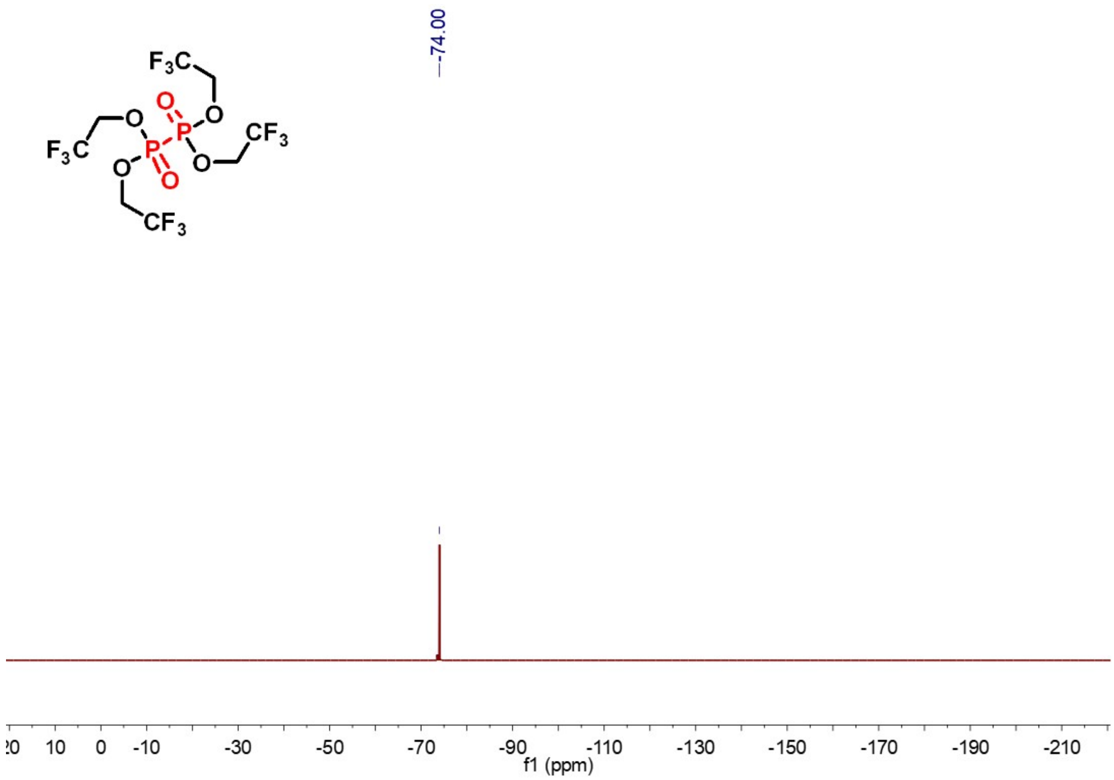


^{13}C NMR (101 MHz) Spectrum of 2l in DMSO-d⁶





^{19}F NMR (376 MHz) Spectrum of 2l in DMSO-d^{6}



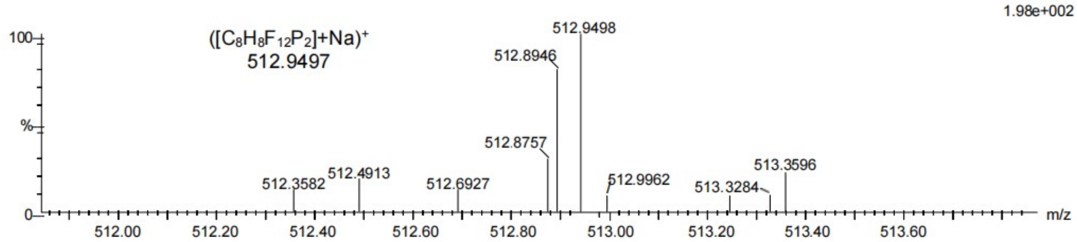
HRMS Spectrum of 2l

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 50.0 PPM / DBE: min = -50.0, max = 500.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

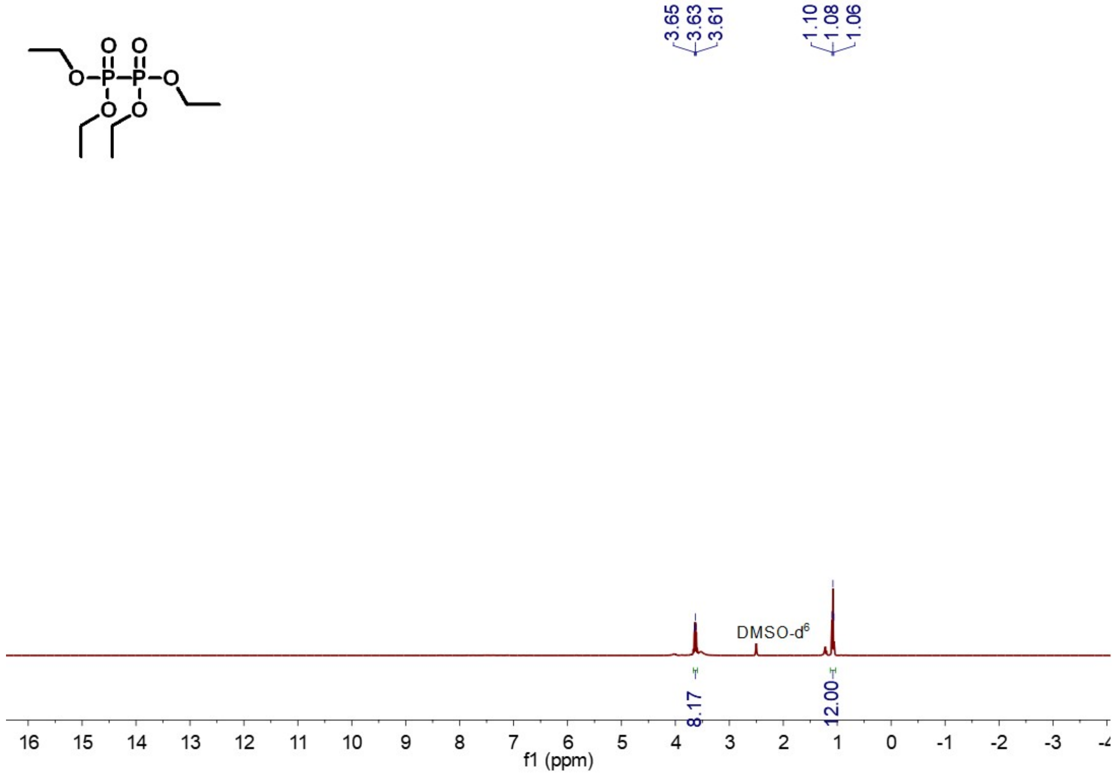
Monoisotopic Mass, Even Electron Ions
9 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 8-8 H: 3-140 O: 1-9 F: 12-12 P: 2-2 Na: 1-1

46
251024--2---1 26 (0.161) 1: TOF MS ES+
1.98e+002

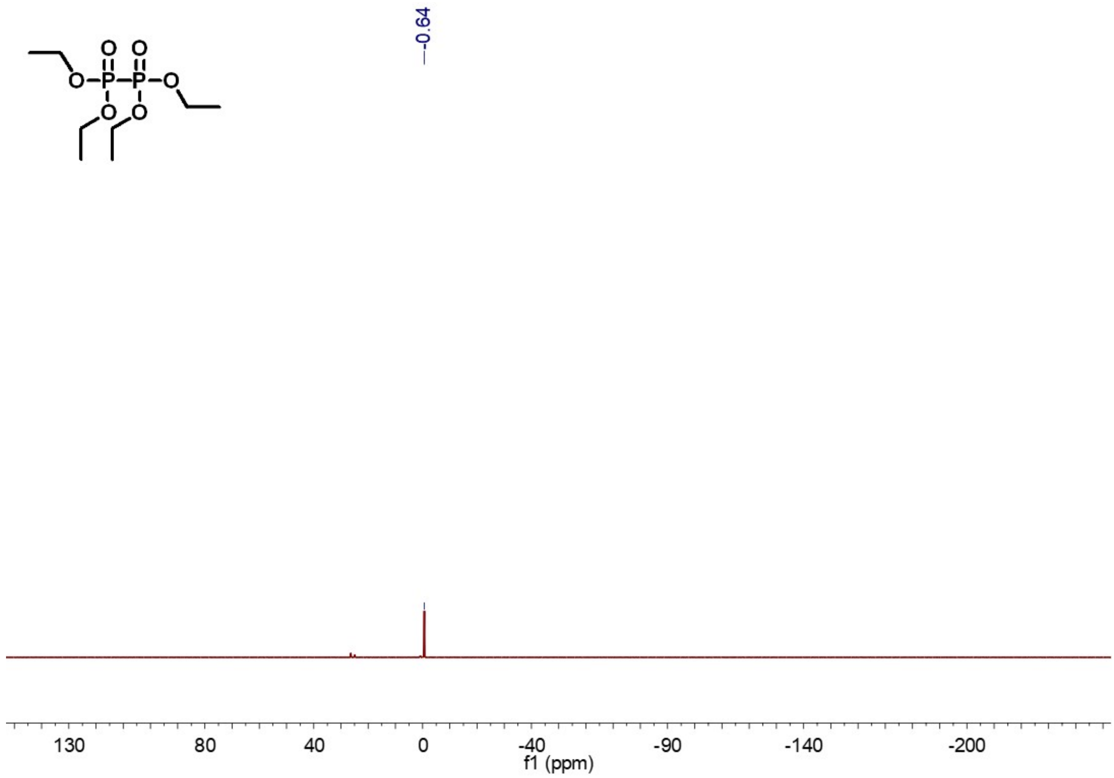


Minimum:				-50.0				
Maximum:		5.0	50.0	500.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
512.9497	512.9502	-0.4	-0.8	-0.5	43.3	n/a	n/a	C8 H8 O6 F12 P2 Na

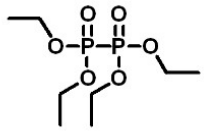
^{1}HNMR (400 MHz) Spectrum of 2m in DMSO-d^{6}

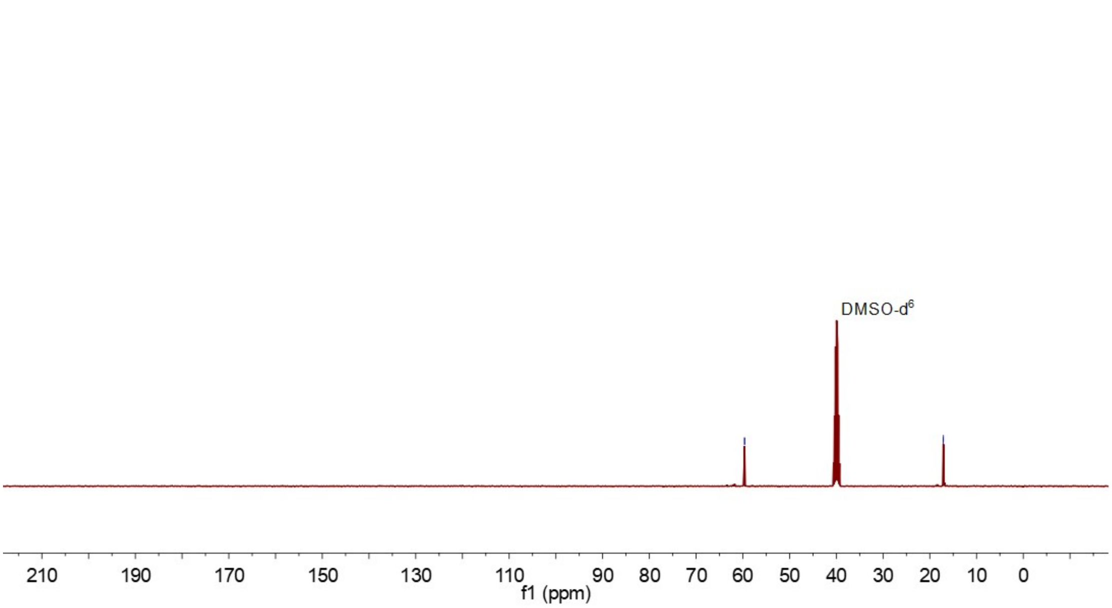


^{31}P NMR (162 MHz) Spectrum of 2m in DMSO-d^{6}

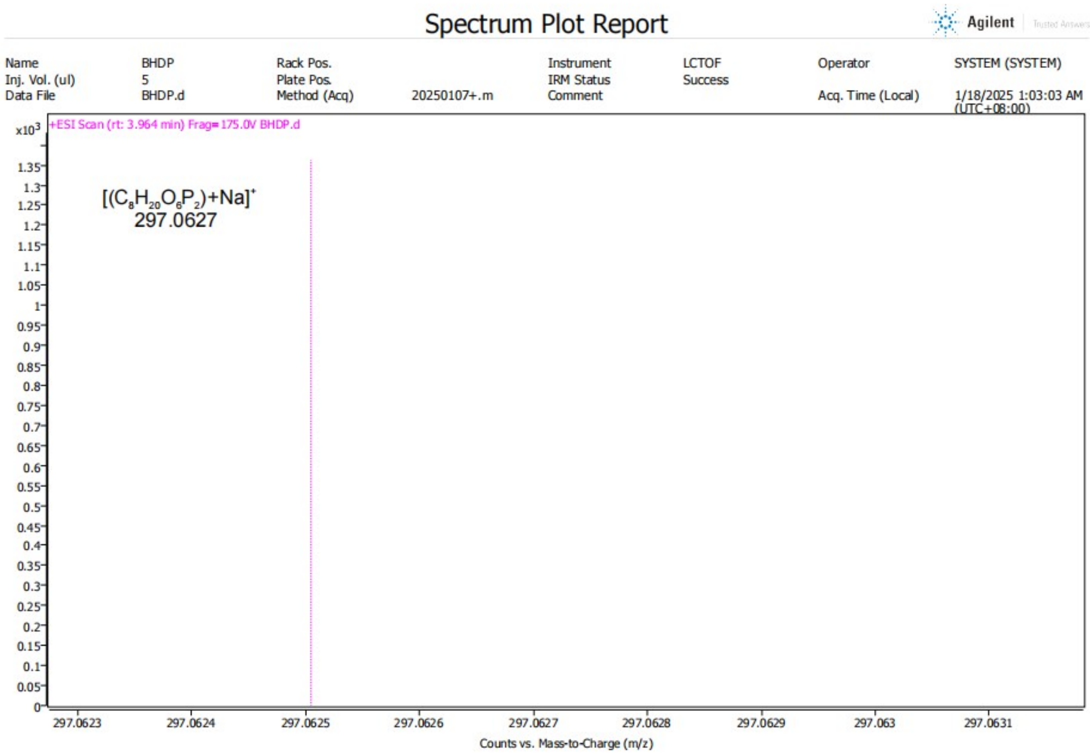


^{13}C NMR (101 MHz) Spectrum of 2m in DMSO-d⁶

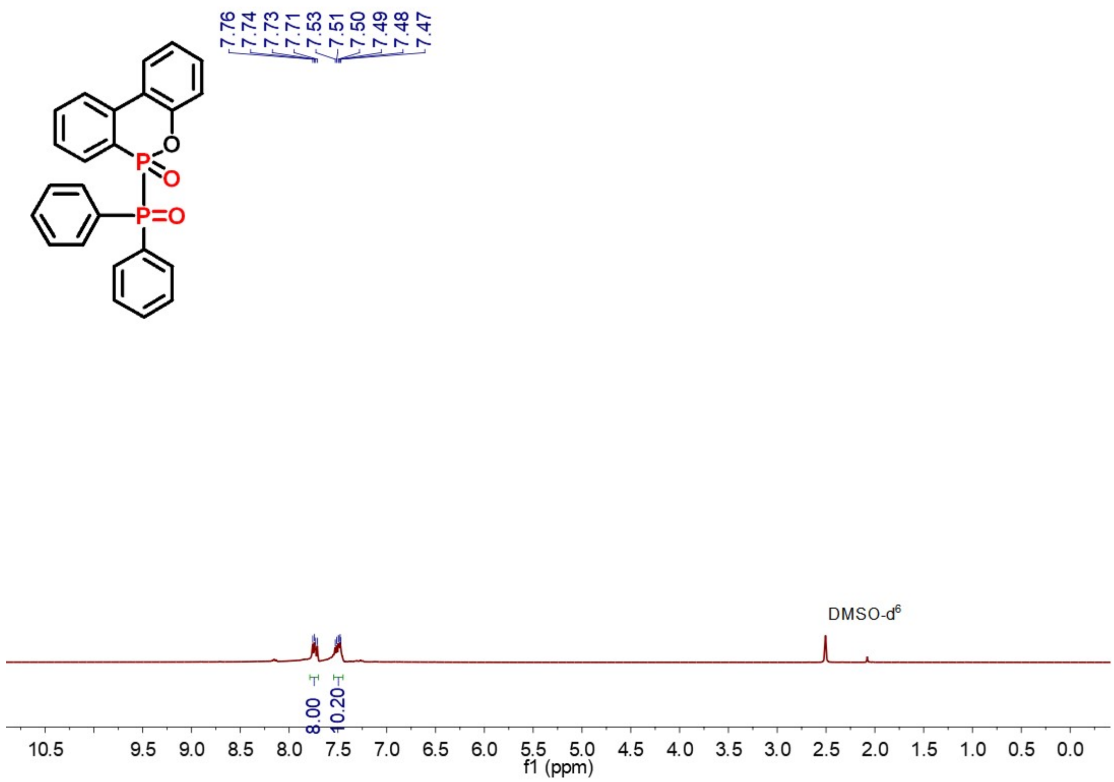




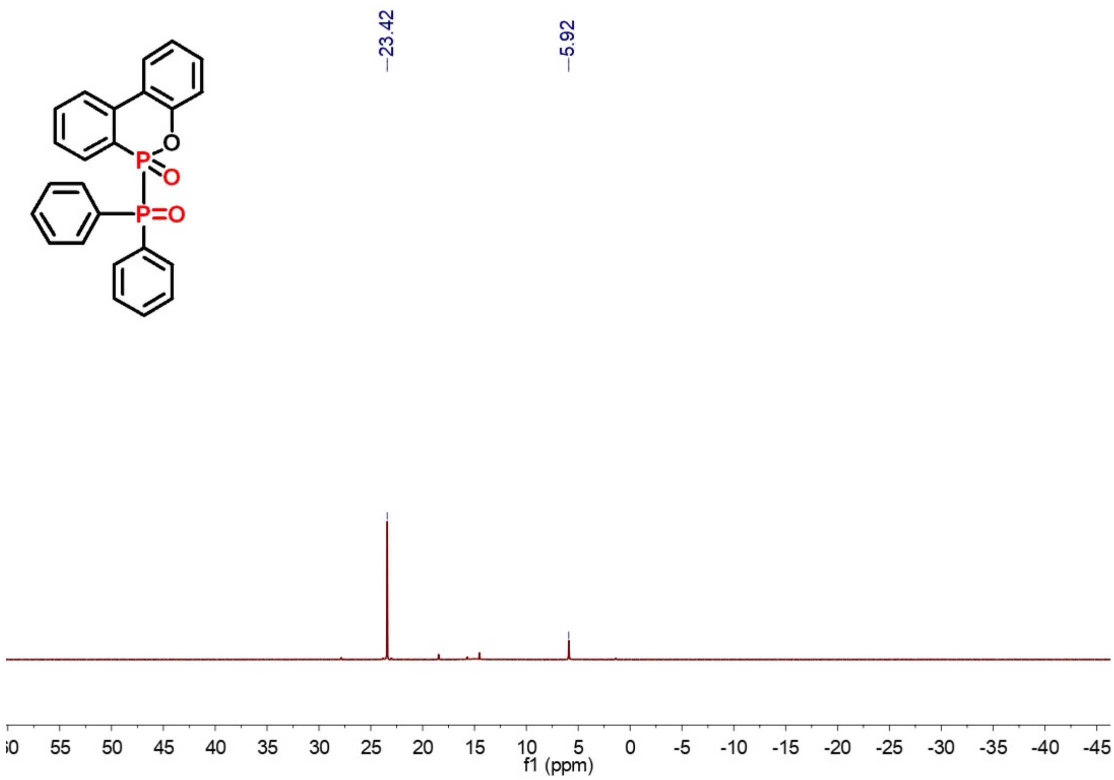
HRMS Spectrum of 2m



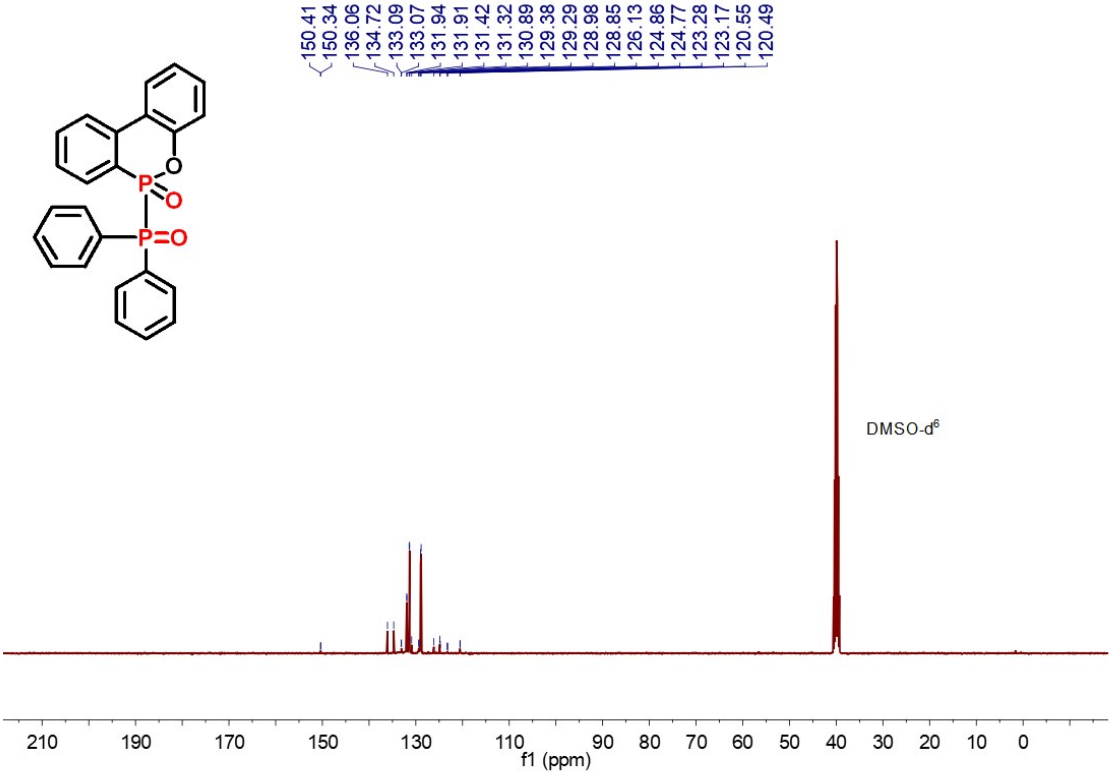
^{1}HNMR (400 MHz) Spectrum of 4a in DMSO-d^{6}



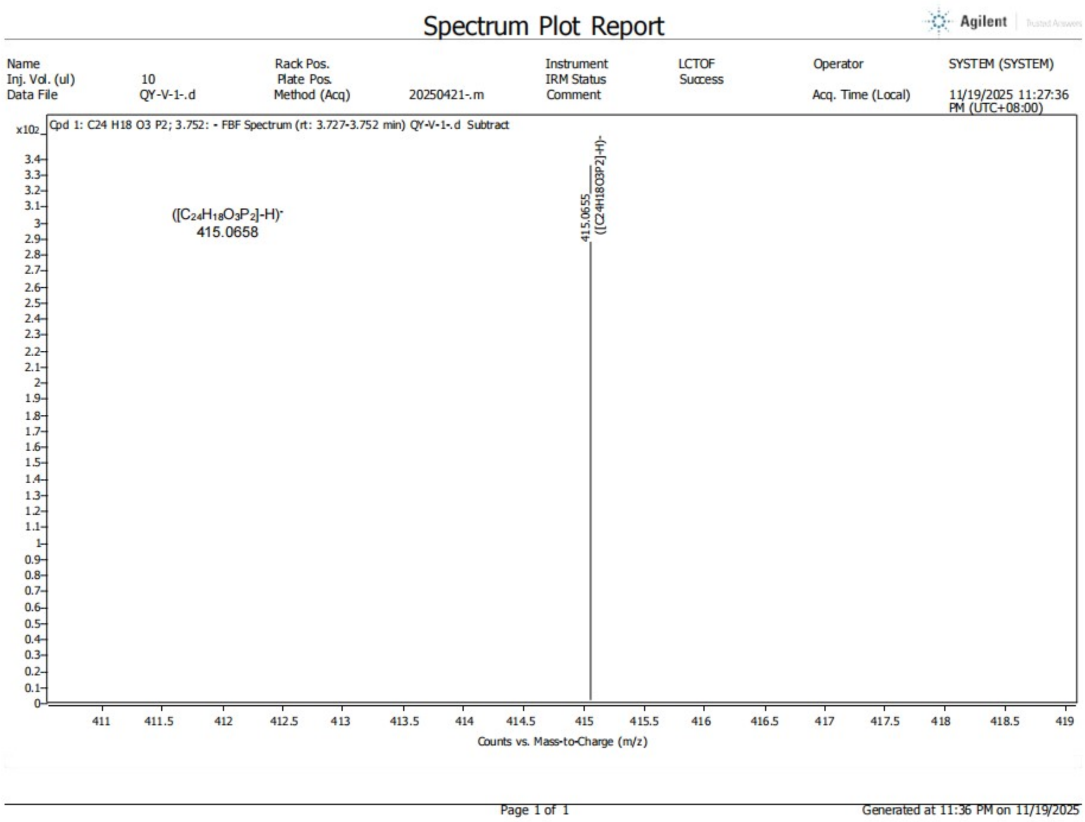
^{31}P NMR (162 MHz) Spectrum of 4a in DMSO-d^{6}



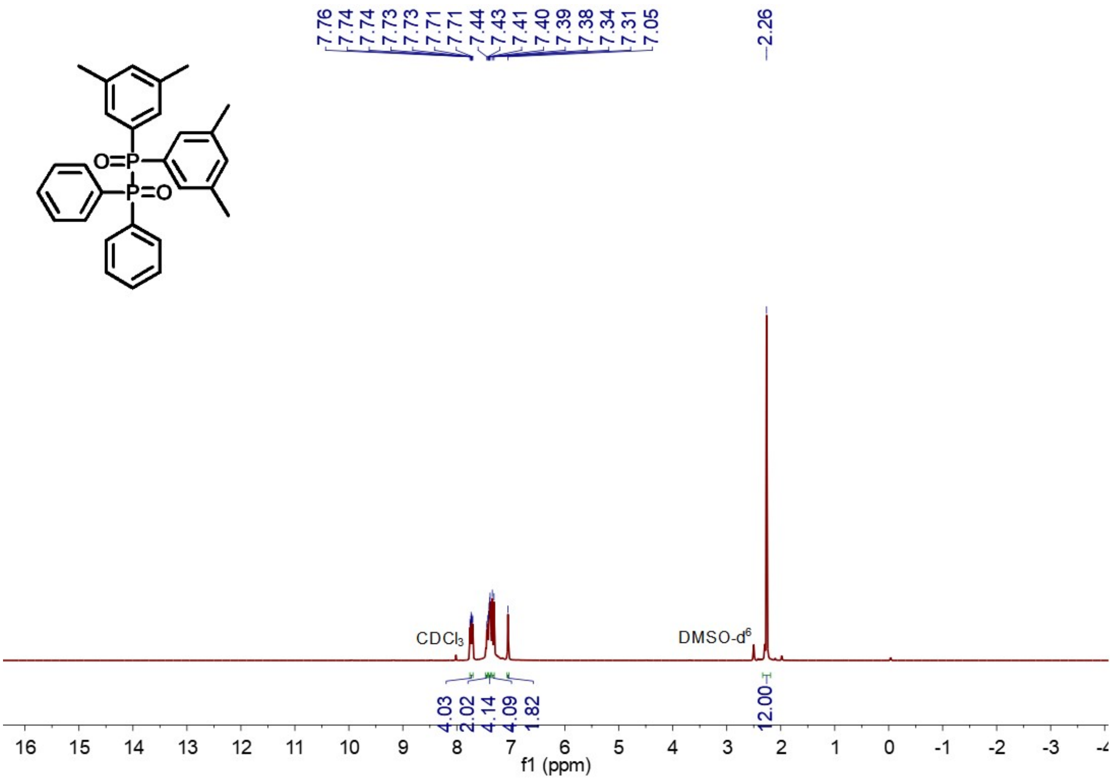
^{13}C NMR (101 MHz) Spectrum of 4a in DMSO-d^6



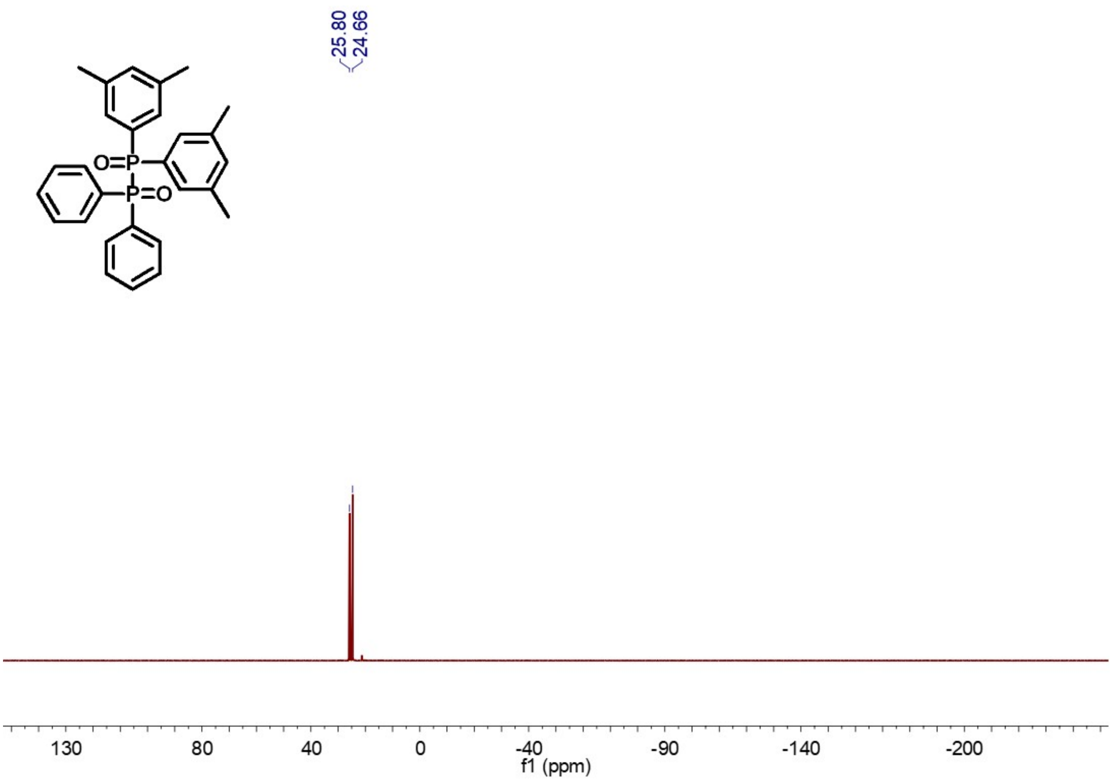
HRMS Spectrum of 4a



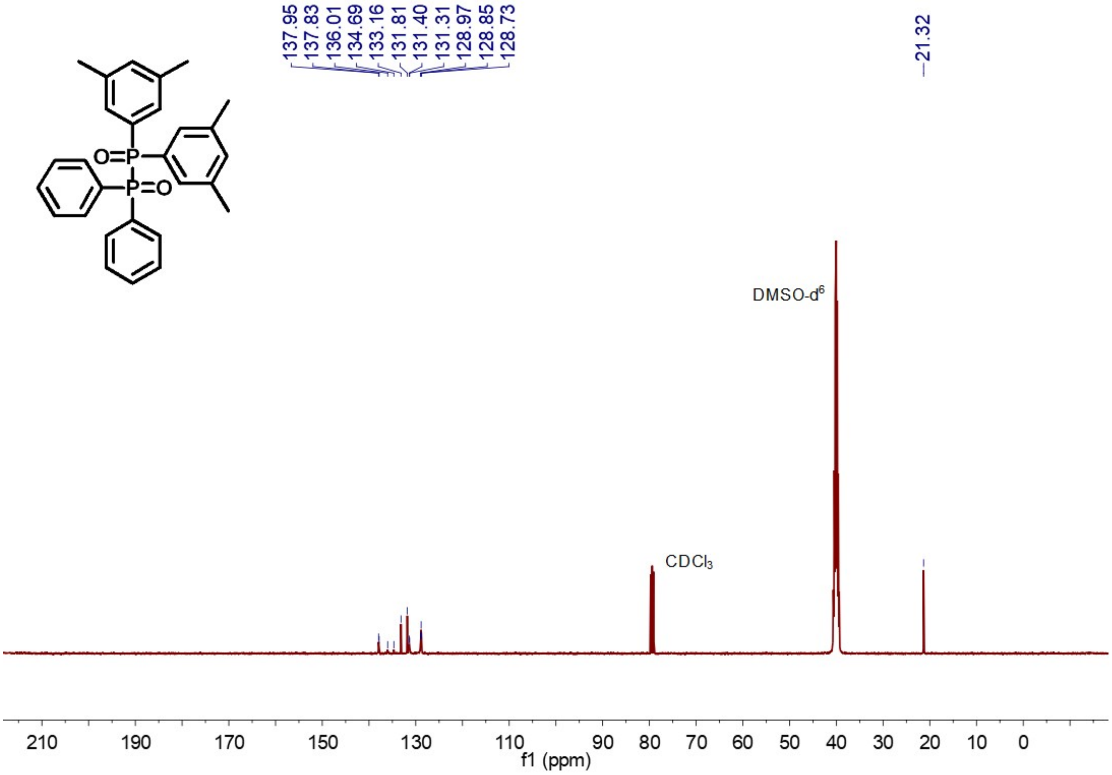
[1]HNMR (400 MHz) Spectrum of 4b in DMSO-d[6]



[31]P NMR (162 MHz) Spectrum of 4b in DMSO-d[6]



^{13}C NMR (101 MHz) Spectrum of 4b in DMSO-d6

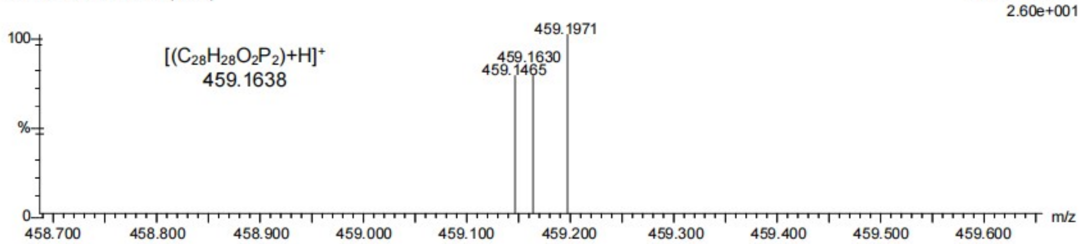


HRMS Spectrum of 4b

Elemental Composition Report **Page 1**

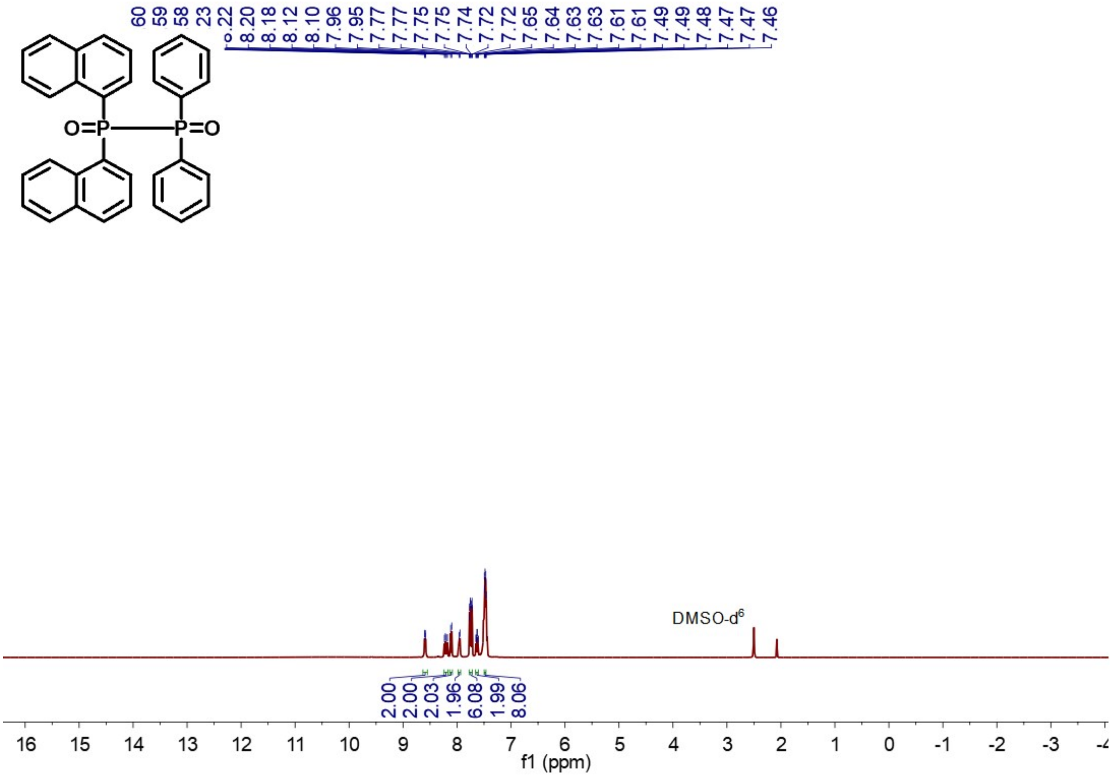
Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
365 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 28-28 H: 29-29 N: 0-100 O: 0-100 P: 2-2
1
251204-13--QY-G-2 13 (0.093) 1: TOF MS ES+ 2.60e+001

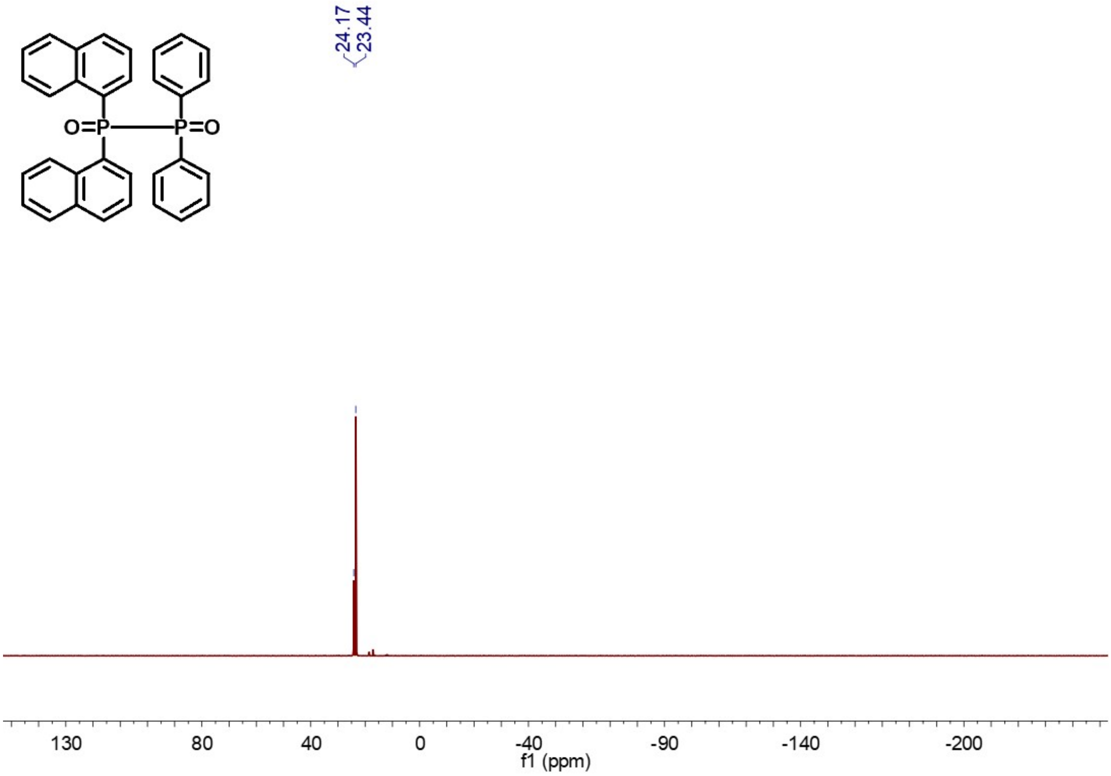


Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
459.1639	459.1643	-0.4	-0.9	15.5	20.2	n/a	n/a	C28 H29 O2 P2

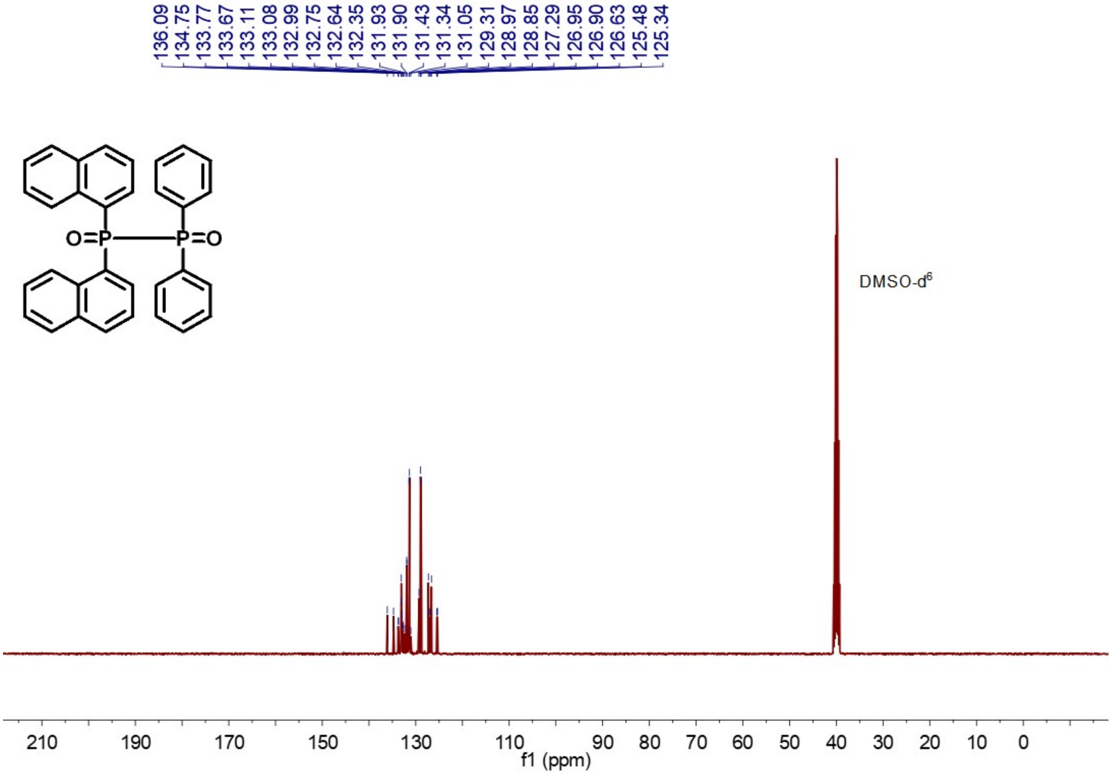
[1]HNMR (400 MHz) Spectrum of 4c in DMSO-d6



[31]P NMR (162 MHz) Spectrum of 4c in DMSO-d6



^{13}C NMR (101 MHz) Spectrum of 4c in DMSO-d[6]

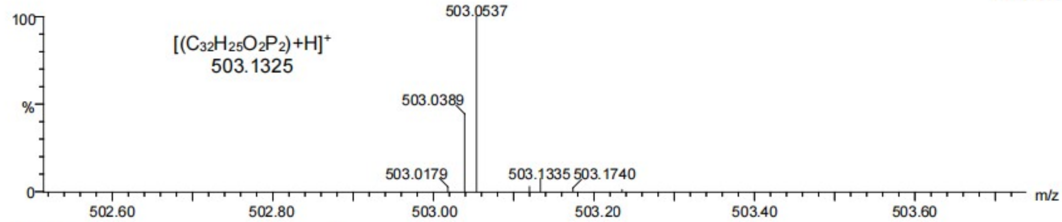


HRMS Spectrum of 4c

Elemental Composition Report **Page 1**

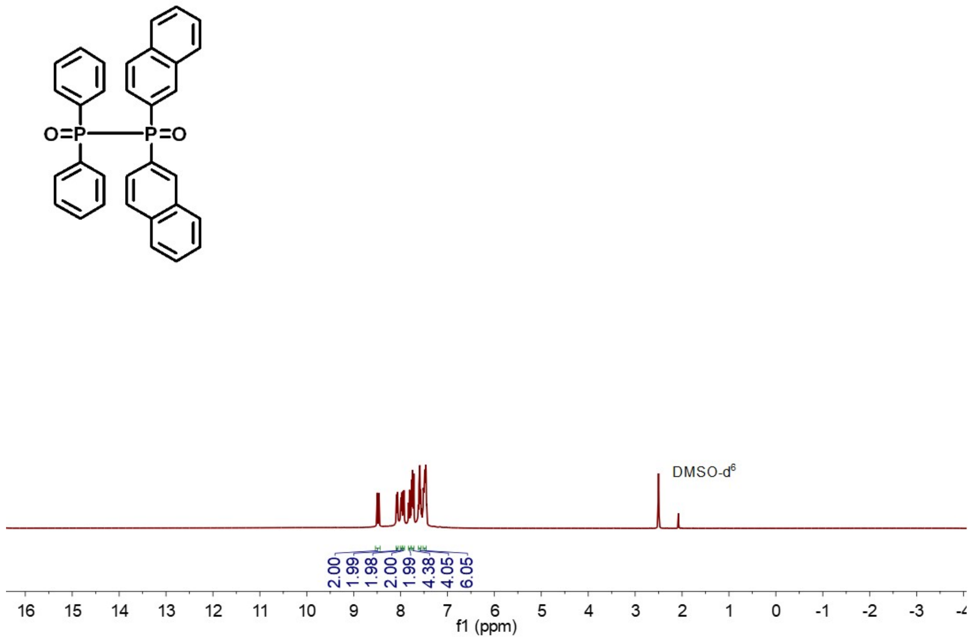
Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
2632 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 32-32 H: 25-25 N: 0-100 O: 0-100 Na: 0-2 P: 1-2
1
251204-13--QY-G-39 (0.072) 1: TOF MS ES+
1.71e+003

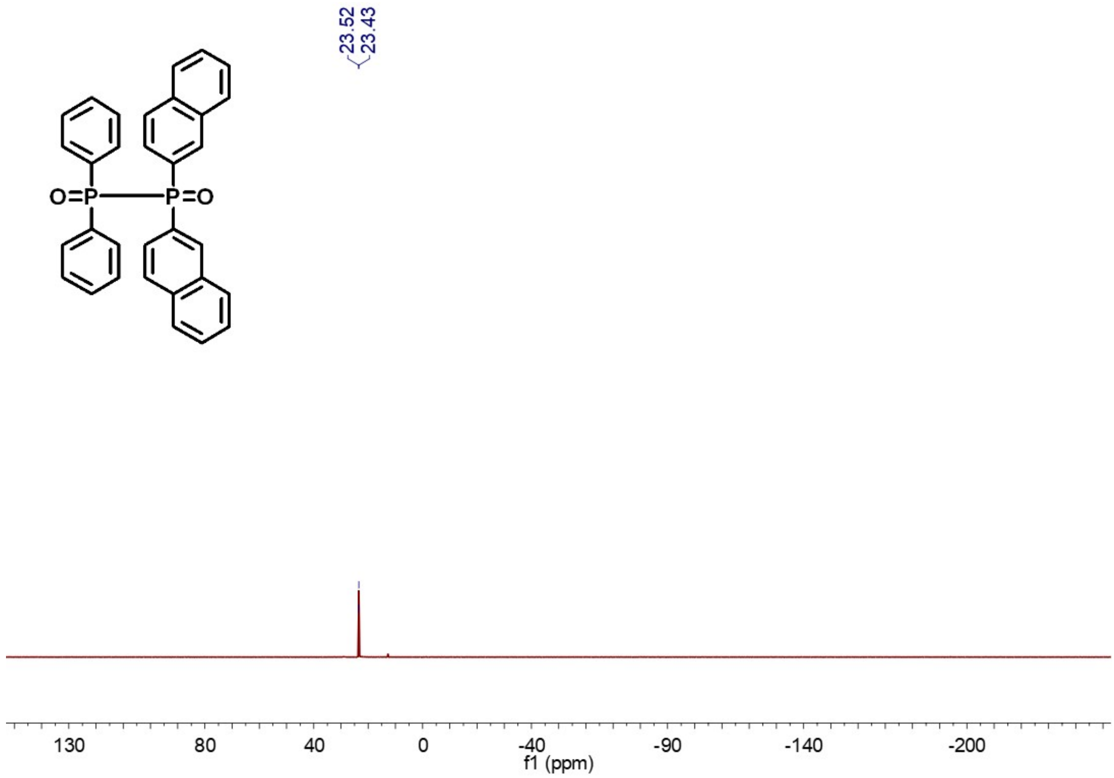


Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
503.1335	503.1330	0.5	1.0	21.5	32.2	n/a	n/a	C32 H25 O2 P2

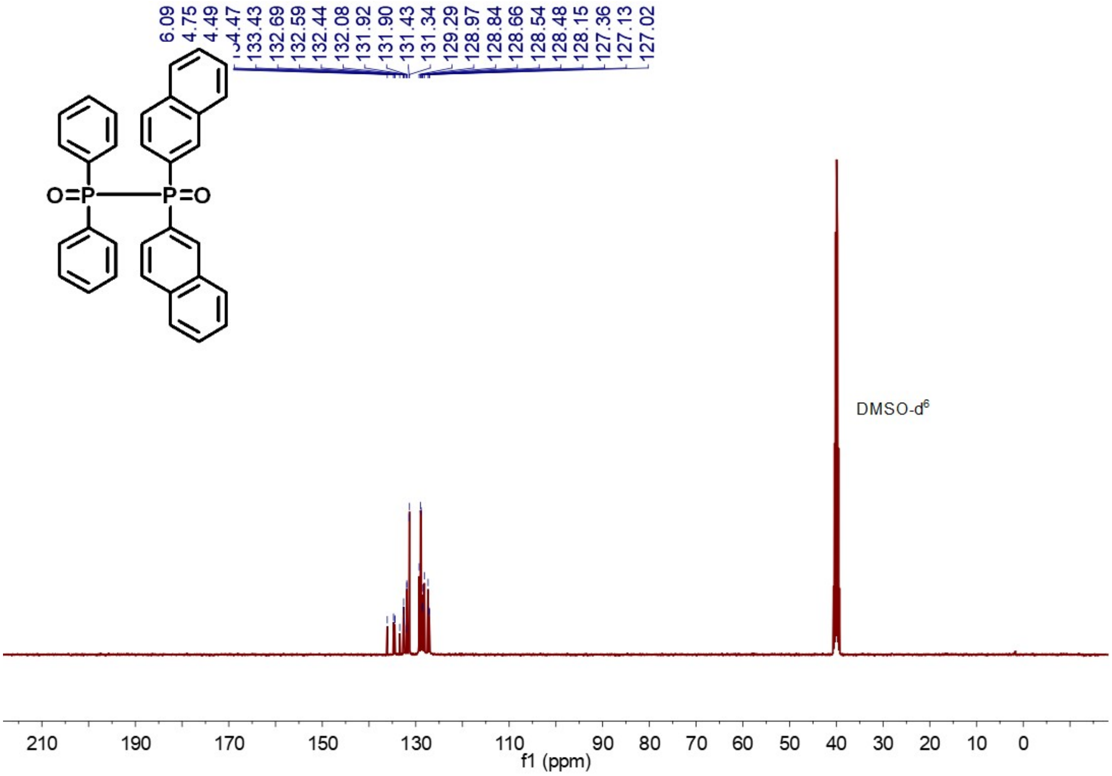
^{1}HNMR (400 MHz) Spectrum of 4d in DMSO-d^{6}



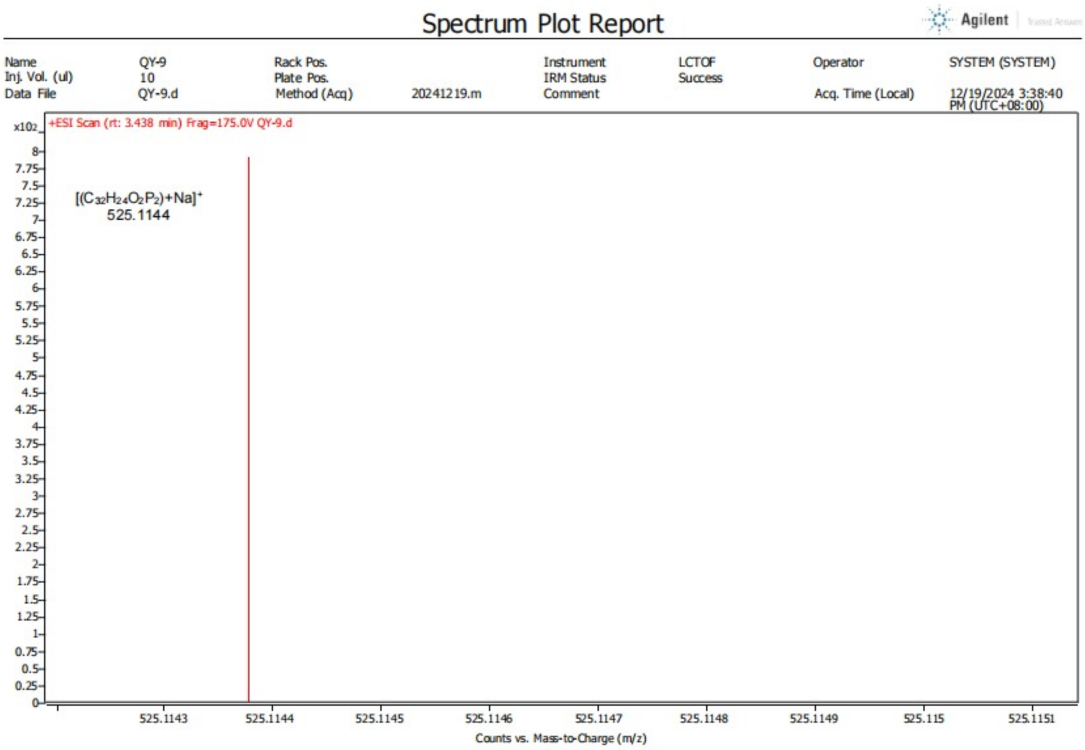
^{31}P NMR (162 MHz) Spectrum of 4d in DMSO-d^{6}



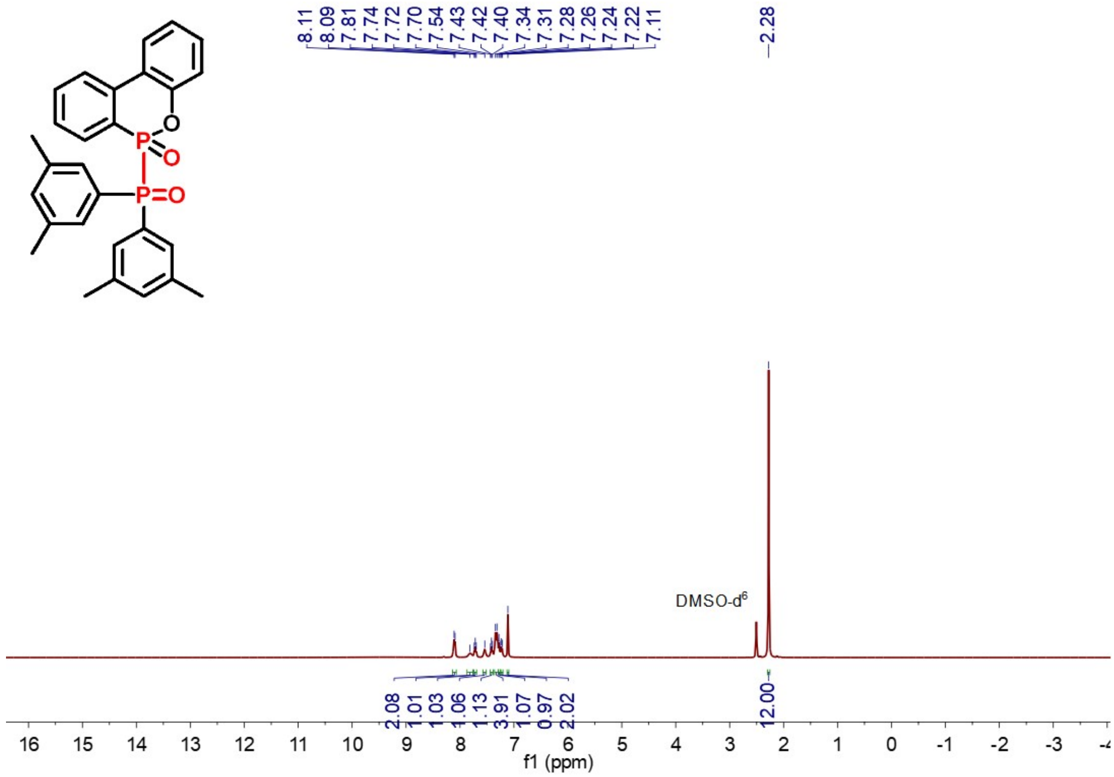
^{13}C NMR (101 MHz) Spectrum of 4d in DMSO-d^6



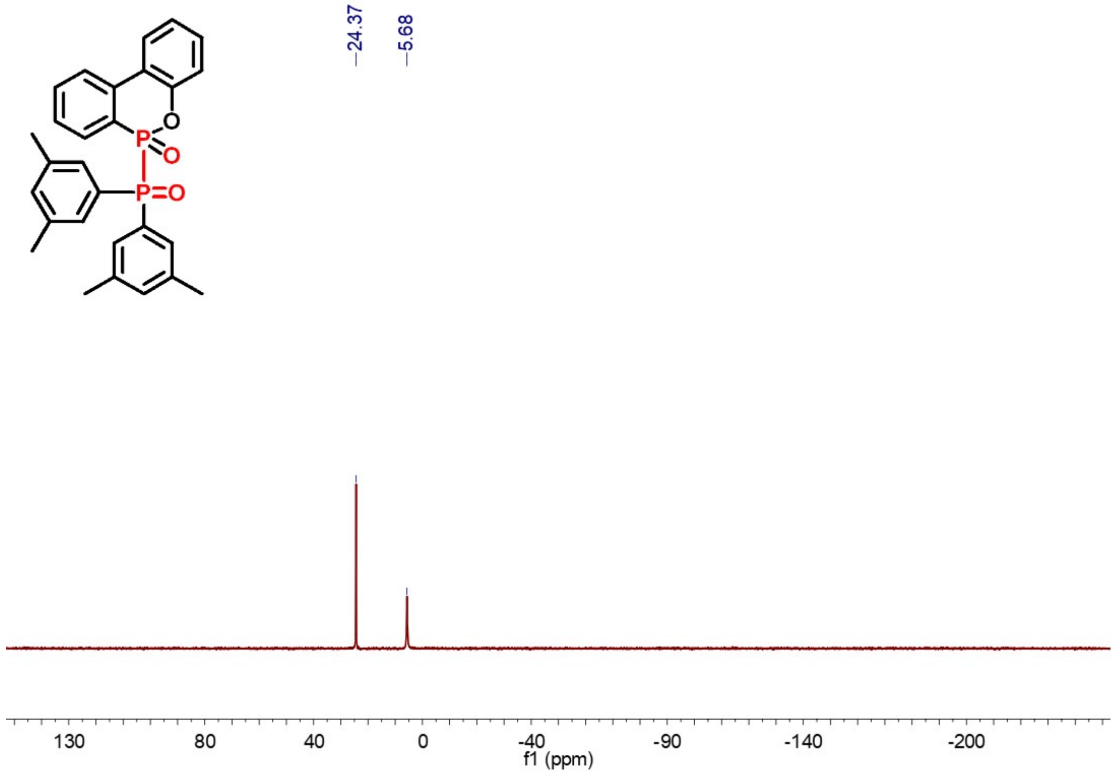
HRMS Spectrum of 4d



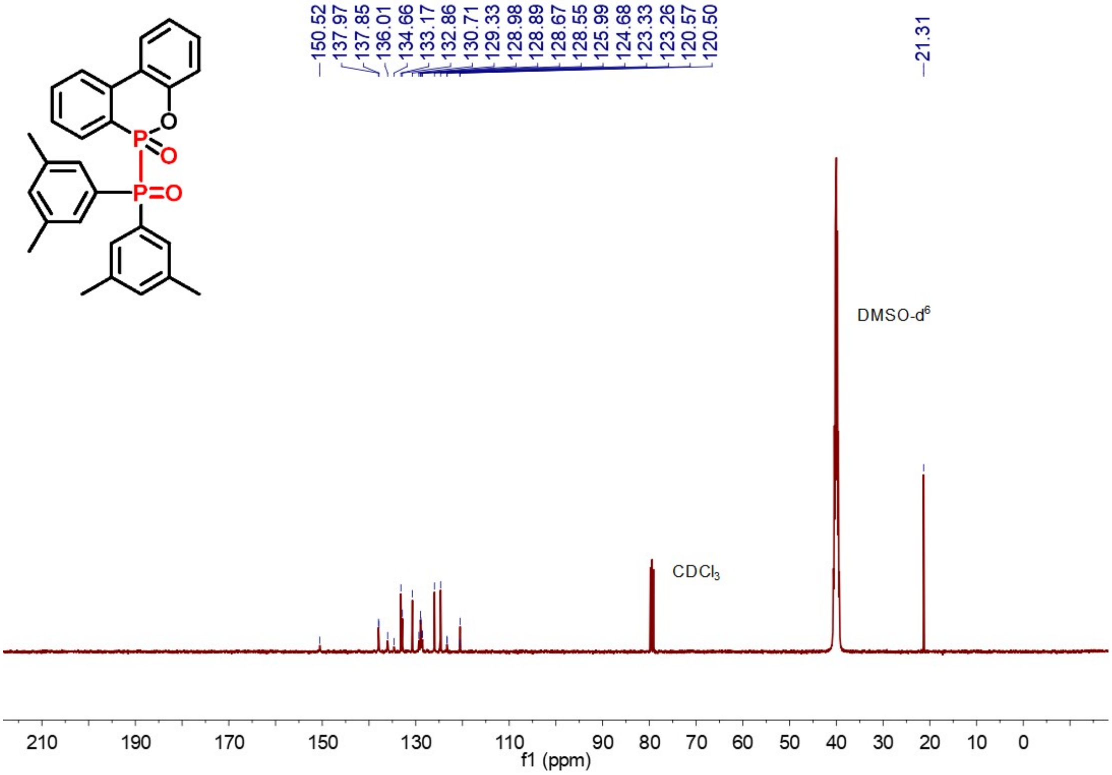
^{1}HNMR (400 MHz) Spectrum of 4e in DMSO-d^6



^{31}P NMR (162 MHz) Spectrum of 4e in DMSO-d^6



^{13}C NMR (101 MHz) Spectrum of 4e in DMSO-d^{6}



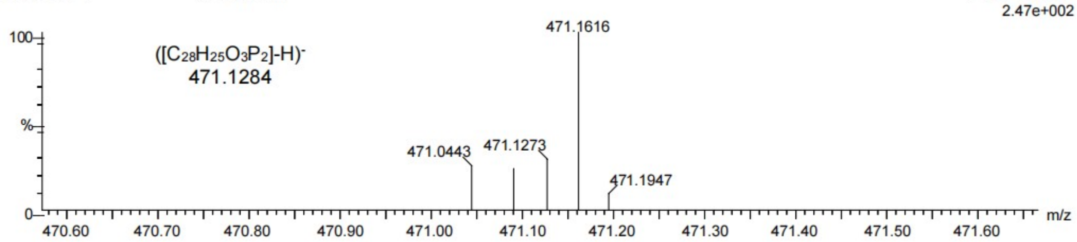
HRMS Spectrum of 4e

Elemental Composition Report **Page 1**

Single Mass Analysis

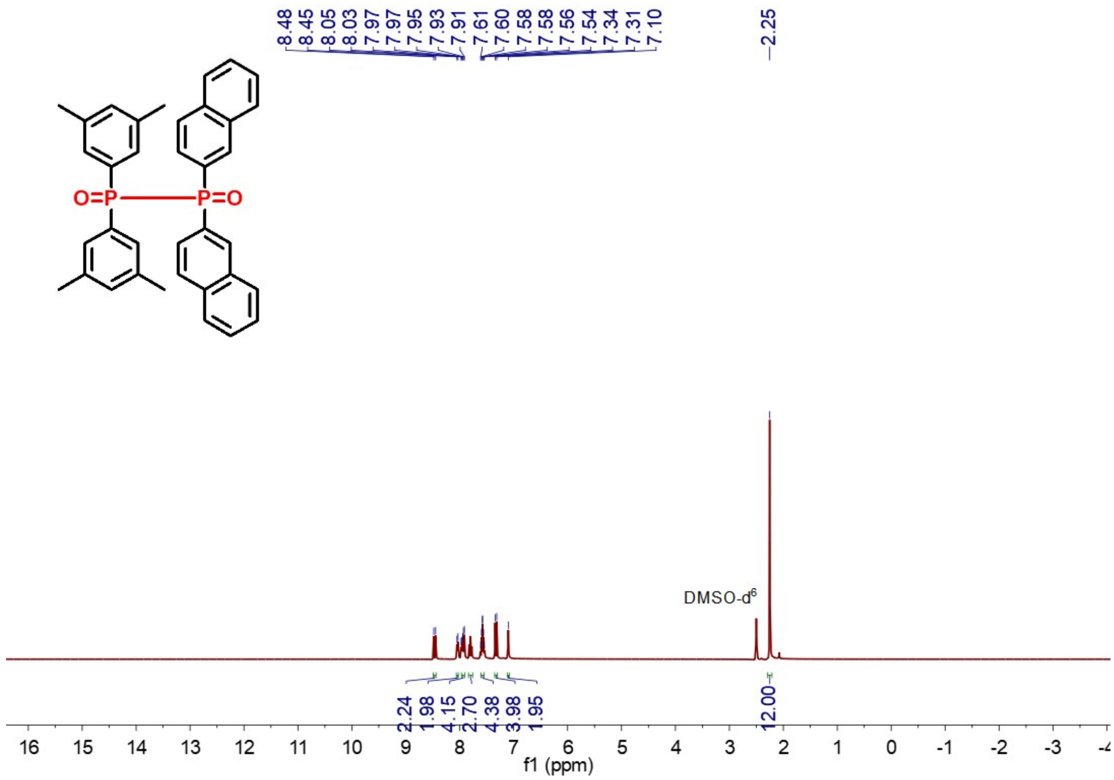
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
1149 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 28-28 H: 25-25 N: 0-100 O: 0-100 P: 1-3
42--P--N
251126-10-1--------------------n 29 (0.282) 1: TOF MS ES- 2.47e+002

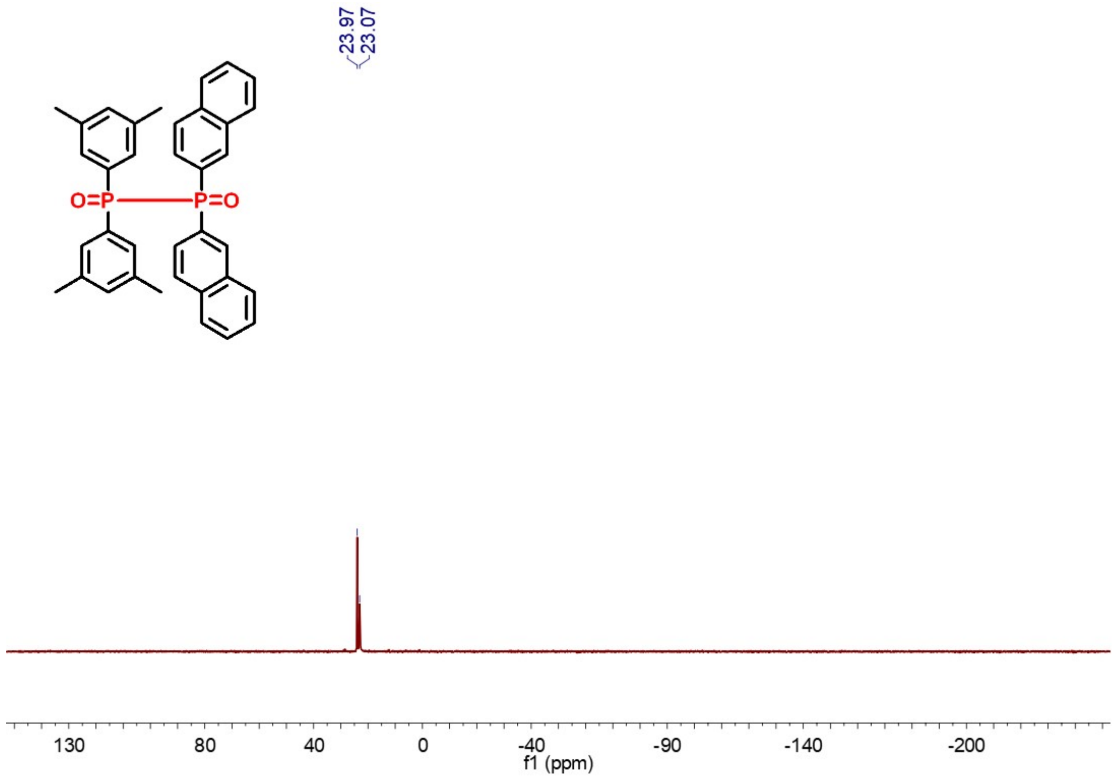


Minimum:				-1.5					
Maximum:		5.0	10.0	50.0					
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula	
471.1284	471.1273	-0.6	-1.3	17.5	34.7	n/a	n/a	C28 H25 O3 P2	

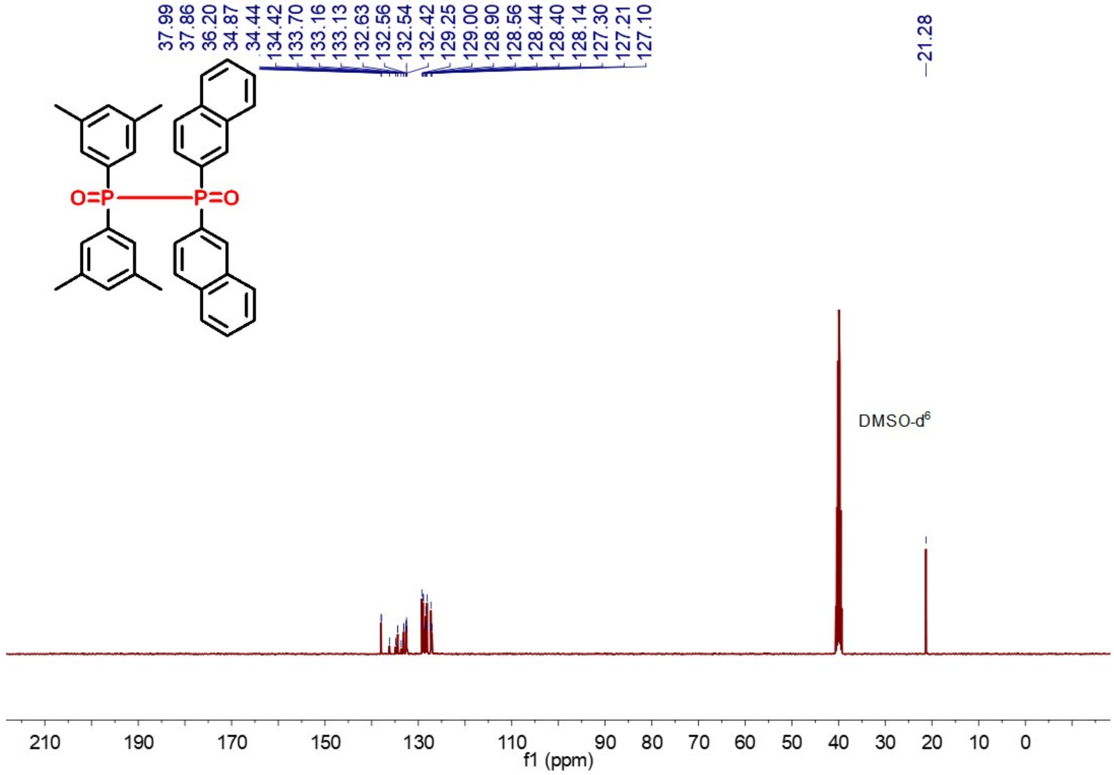
[1]HNMR (400 MHz) Spectrum of 4f in DMSO-d[6]



[31]P NMR (162 MHz) Spectrum of 4f in DMSO-d[6]



[13]C NMR (101 MHz) Spectrum of 4f in DMSO-d[6]



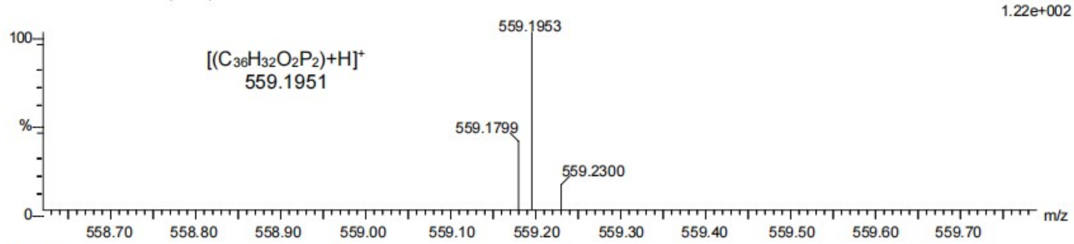
HRMS Spectrum of 4f

Elemental Composition Report **Page 1**

Single Mass Analysis

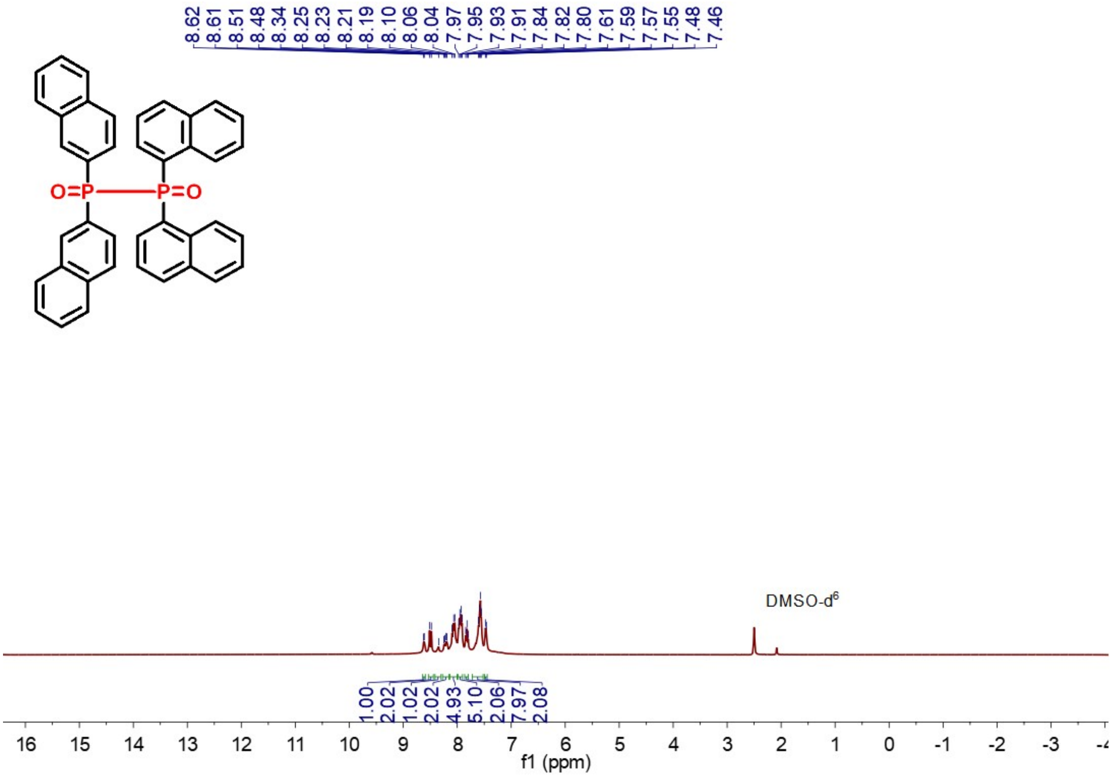
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
571 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 36-36 H: 33-33 N: 0-100 O: 0-100 P: 2-2
1
251204--13--QY-G-2 17 (0.114) 1: TOF MS ES+ 1.22e+002

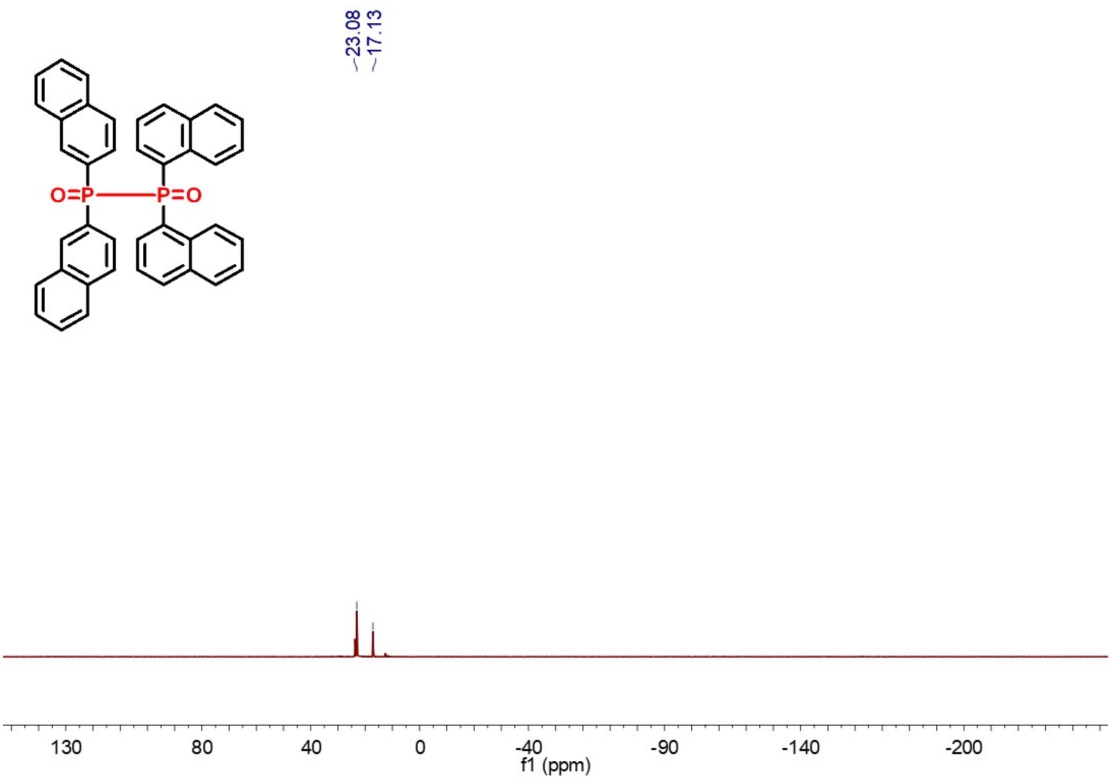


Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
559.1953	559.1956	-0.3	-0.5	21.5	25.1	n/a	n/a	C36 H33 O2 P2

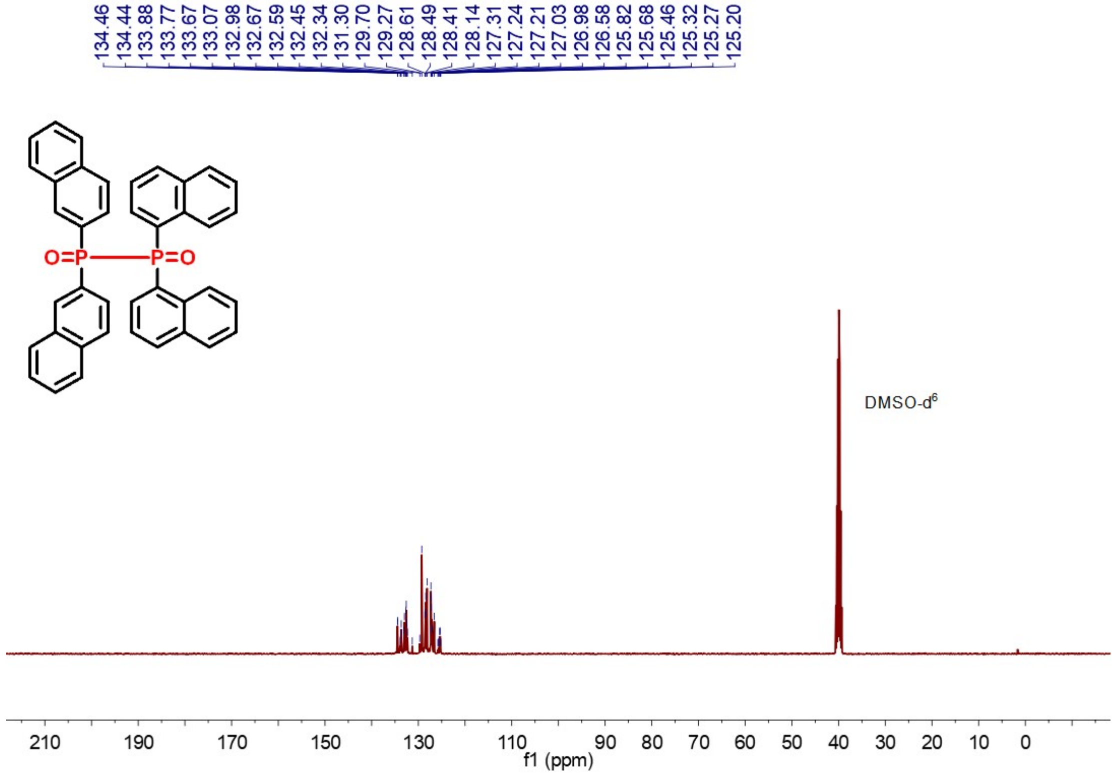
^{1}HNMR (400 MHz) Spectrum of 4g in DMSO-d^{6}



^{31}P NMR (162 MHz) Spectrum of 4g in DMSO-d^{6}



^{13}C NMR (101 MHz) Spectrum of 4g in DMSO-d6



HRMS Spectrum of 4g

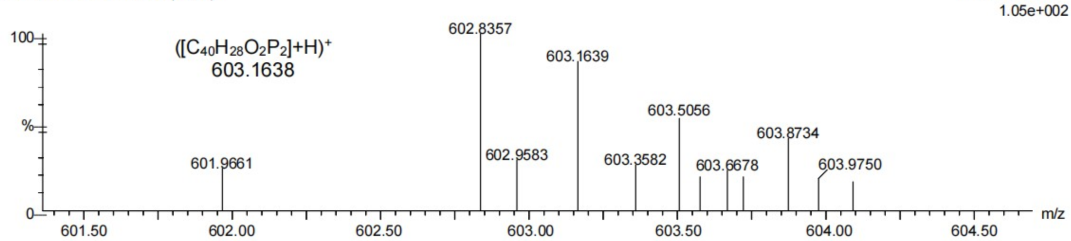
Elemental Composition Report **Page 1**

Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
676 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 40-40 H: 29-29 N: 0-100 O: 0-100 P: 2-2

1
251204--13--QY-G-1 44 (0.264) 1: TOF MS ES+
1.05e+002



Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
603.1639	603.1643	-0.4	-0.7	27.5	68.8	n/a	n/a	C40 H29 O2 P2